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Development of an Efficient Sampling Strategy
to Characterize Digested Sludges

Research Report No. 71

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DEVELOPMENT OF AN EFFICIENT SAMPLING
STRATEGY TO CHARACTERIZE DIGESTED SLUDGES

by

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ABSTRACT

Anaerobically digested liquid sludges from five Ontario water pollution control plants were examined to identify the sources of constituent variability (nutrients, heavy metals, physical characteristics) by determining whether variations arose from sample handling and methods of analysis, from changes in composition with time, or from inherent sludge heterogeneity. Familiar methods of data reduction (graphical time sequences, probability plots, averages, confidence limits, etc.) have been combined with more rigorous methods of data analysis (analysis of variance, time series analysis) to assist in data interpretation. The results are fundamental for establishing efficient sampling programs to monitor nutrient and undesirable contaminant discharges in sludges destined for disposal.

The greatest variability occurred within an operating day at plants hauling tank truck batches to disposal sites and at plants dewatering sludge. Variability between days was usually less than within day variability. Plants with dewatering devices processed a more homogeneous liquid sludge than plants using truck haulage.

Checks at one plant showed that significant changes had occurred in sludge parameter concentrations after five months. At a second plant, where sludge was monitored each weekday for five months, ammonia and nickel were the least variable parameters; in the same time interval other heavy metals and total solids reached independent peak concentrations.

Two years' total solids records for raw and digested sludges from two plants were examined using time series analysis. At one plant, the time series and its autocorrelation function suggested that neighbouring samples were similar, and that trends existed within the record. At the second plant, variations were random. All series were stationary with fixed means.

It is recommended that plants disposing sludge by tank trucks monitor the quality of each batch separately on a sampling day; a composite sample must be taken from the input to the tank trucks. The

precision in mean concentrations for various constituents can then be expected to be in the approximate range ±7 to ±55% within a batch with sampling at approximately two-week intervals. The greater precision (±7%) is associated with liquid phase constituents. Precisions in the range ±5 to ±16% can be achieved at plants continually withdrawing sludge to dewatering devices if a one-day composite sample is collected once every two weeks. For ammonia, one grab sample every two weeks is sufficient to estimate the mean concentration within about ±10% at either type of plant.

Residence time distribution studies indicated that primary and secondary digesters were inefficiently mixed, with only about 25% of primary digesters in the active mix state. Short circuiting was also a problem.

An ammonia gas sensing electrode was found to be fast, accurate and suitable for field determinations in the range found in sludge (100 to 1500 mg·l^{-1}).

RÉSUMÉ

Les boues liquides digérées par voie anaérobie de cinq stations
de traitement de l'eau de l'Ontario ont été étudiées en vue de déterminer
les causes de la variation de leurs caractéristiques (teneur en éléments
nutritifs, en métaux lourds et caractéristiques physiques). Il s'agissait
d'établir si ces variations étaient attribuables à la manipulation des
échantillons et aux méthodes d'analyse, à l'action du temps, ou à
hétérogénéité naturelle des boues. Les méthodes courantes de réduction des
données (représentation graphique des séries chronologiques, diagramme de
probabilités, calcul des moyennes et des limites de confiance, etc.) ont
été combinées à des méthodes plus rigoureuses (analyse de la variance et
des séries chronologiques) pour faciliter l'interprétation des données.
Ces résultats sont essentiels à l'établissement de programmes d'échantil-
lonnage aptes à contrôler la quantité d'éléments nutritifs et de polluants
dans les boues à éliminer.

Les plus grandes variations à l'intérieur d'une même journée
d'exploitation se sont produites aux installations envoyant leurs boues
en décharge par camions-citernes et aux installations faisant l'essorage
des boues. Les variations d'une journée à l'autre étaient habituellement
moindres qu'au cours d'une même journée. Les boues liquides manutentionnées
dans les installations les essorant étaient plus homogènes qu'aux
installations les envoyant en décharge.

Des contrôles à l'une des installations ont montré que les
caractéristiques chimiques des boues s'étaient modifiées sensiblement
aprés cinq mois. A une autre installation, où les contrôles se sont
faits quotidiennement pendant cinq mois, ce sont les teneurs en ammoniac
et en nickel que ont le moins varié, tandis que la teneur en autres métaux
lourds ainsi qu'en matières solides a atteint des maximums distincts.

Les relevés, sur deux années, de la teneur en matières solides
totales des boues fraîches et digérées de deux installations ont servi à
établir des séries chronologiques. Pour l'une des installations, il a
été établi, d'après la série chronologique et sa fonction d'autocorrélation,
que les échantillons de périodes voisines s'équivalaient et qu'il se
dégageait certaines tendances. En ce qui concerne la deuxième installation,

les variations étaient dues au hasard. Toutes les séries sont demeurées stationnaires et leurs moyennes fixes.

Il est à souhaiter que les installations qui éliminent leurs boues par camoins-citernes contrôlent la qualité de chaque lot durant la même journée d'échantillonnage; il apparaît nécessaire de prélever un échantillon composé au moment du chargement des camions. Il est ainsi possible d'obtenir des concentrations moyennes de constitutants d'une précision qui varie entre ±7 et ±55% pour un lot échantilloné environ toutes les deux semaines. La précision la plus grande (±7%) s'obtient avec les constituants en phase liquide. En prélevant un échantillon toutes les deux semaines, la précision est de l'ordre de ±5 à ±16% dans le cas d'installations que envoient en continu leurs boues dans des appareils d'essorage. Pour évaluer la concentration de l'ammoniac avec une marge d'erreur de ±10% aux deux genres d'installation, il suffit d'un seul échantillonnage au hasard toutes les deux semaines.

Les études sur la répartition des boues durant leur temps de séjour ont montré que le mélange dans les digesteurs primaires et secondaires était inefficace, le digesteur primaire n'activant que 25% des boues. Les courts-circuits ont aussi constitué un problème.

L,électrode spécifique à l'ammoniac a été rapide, exacte et propre à déterminer sur le terrain la teneur du gaz dans les boues (entre 100 et 1500 mg/l).

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NOMENCLATURE

ACF	-	autocorrelation function
ANOVA	-	analysis of variance
C	-	concentration
C_0	-	expected initial concentration
CCF	-	cross correlation function
CL	-	confidence limit (95%)
HOAc	-	acetic acid
MIGD	-	million gallons per day (Imperial)
MOE	-	Ministry of Environment, Ontario
MS	-	mean square
NH_3-N	-	ammonia, expressed as nitrogen
PACF	-	partial autocorrelation function
RSD	-	relative standard deviation
RTD	-	residence time distribution
SS	-	sum of squares
TDS	-	total dissolved solids
TKN	-	total Kjeldahl nitrogen
TOC	-	total organic carbon
TP	-	total phosphorus
TS	-	total solids
V	-	total volume
V_a	-	volume involved in active mixing
V_d	-	dead volume
VS	-	volatile solids
WPCP	-	water pollution control plant
$\bar{d}$	-	average difference between two measurements
df	-	degrees of freedom
k_{ij}	-	auxiliary quantity
ℓ	-	stipulated precision of mean, $\bar{x}$
n	-	sample size
r_k	-	autocorrelation coefficient
$r_{xy}(k)$	-	cross correlation coefficient
s	-	sample standard deviation
$\bar{x}$	-	sample mean

NOMENCLATURE (CONT'D)

Greek Letters

γ_{ij} -   gamma, auxiliary quantity

δ -   delta, Dirac delta function

θ -   theta, hydraulic residence time $= \dfrac{V}{\upsilon}$

μ -   mu, population mean

σ -   sigma, population standard deviation

υ -   upsilon, flow rate

$\hat{\phi}_{kk}$ -   phi, partial autocorrelation coefficient

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

This investigation was performed to estimate the degree of variability in the physical-chemical characteristics of liquid sludge discharged from anaerobic digesters. Constituent concentrations measured included: TKN, NH_3-N, TP, Fe, Ni, Cu, Zn, Pb, Cd, Al, TOC, TDS, TS, VS. The purpose of these measurements was to aid in the design of efficient sampling programs to monitor process outputs at water pollution control plants. Observations were taken at five Ontario water pollution control plants; each used the conventional activated sludge process. Three plants disposed of liquid sludge by truck haulage to farmland; two plants semi-continuously pumped liquid digested sludge to dewatering devices. The largest plant treated an average of 4.7 MIGD ($21,400 \ m^3 \cdot day^{-1}$) of raw sewage. Sampling programs varied from two-week intervals to five-month intervals. Plant records (TS, VS) for two-year intervals were examined for two of the plants to estimate the characteristics of long term variations, and to obtain an appropriate sampling frequency. The following conclusions have been made:

1. The greatest contribution to digested sludge variability occurred within a single operating day for batch and semi-continuous withdrawal modes. Variability between days was masked by within day variability during two or three-week intervals. Sample handling and analytical testing were usually the smallest sources of variation.

2. A sample, composited from the input to separate tank truck batches, can provide estimates of mean constituent concentrations within each batch with relative precisions in the range ±7 to ±55%; the greater degree of precision is obtained with liquid phase constituents. A limited amount of data indicated that tank truck contents were relatively homogeneous after filling and transit to a disposal site.

3. Multiple batch loads of sludge hauled from a plant within the same sampling day must be monitored separately because there

is a decrease in solid phase constituent concentrations in a sequence of batches. Rapid sludge withdrawal to tank trucks leads to potential channelling in the sludge blanket, and to reduced solids concentration.

4. Variability of liquid sludge sampled at plants which semi-continuously dewatered sludge was approximately one-third the variability observed at plants which discharged by batch truck loads. A composite sample, collected from the feed to a dewatering device during a sampling day, can provide estimates of mean constituent concentrations with relative precisions in the range ±5 to ±16%; the greater degree of precision is obtained with liquid phase constituents. The semi-continuous pumping from the secondary digester to a dewatering device accounted for a decrease in variability.

5. Total solids concentrations from two different plants' records were characterized by means which were constant during two-year intervals. Observations taken at one plant deviated randomly from the mean. Observations at the second plant were not random, but were autocorrelated in time owing to similar variations in the input to the system.

6. Digested sludge total solids concentrations can be efficiently monitored by using a randomly selected one-day sampling program every two weeks at plants practising batch or semi-continuous type sludge withdrawal. It is anticipated that other constituents may also be monitored in this way.

7. Significant changes in constituent concentrations other than total solids occurred during time intervals of several months, and correlation of heavy metal concentrations to total solids concentrations was an unreliable technique for prediction during similar intervals. Heavy metal concentrations were correlated with total solids concentrations during two or three-week time intervals.

8. Some constituents were more variable than others within the sludge at any single plant. Liquid phase constituents (NH_3-N,

TDS) were less variable than solid phase constituents (heavy metals, TKN, TP). NH_3-N can be estimated within approximately ±10% of the mean value at any time at either type of plant.

9. Short circuiting and dead space were observed in two primary digesters, and were considered the result of inefficient mixing. Mixing inefficiency can increase the heterogeneity of the end product, and decrease digestion efficiency.

10. The ammonia gas sensing electrode was found to be a rapid, precise method of determining NH_3-N concentrations in digested sludge at a plant site.

RECOMMENDATIONS

1. Since digested sludge composition varies from plant to plant, sampling must be conducted at individual plants to establish parameter concentrations and variability.

2. Digested sludge quality should be assessed using a frequency of one sampling day per two-week interval. The sampling day should be varied to eliminate daily bias.

3. At plants where sludges are discharged from the digester semi-continuously (i.e., dewatering plants), the sludge sample should be composed of at least three grab samples collected during the sampling day.

4. At plants where sludges are discharged from the digester batchwise (i.e., to tank trucks), each batch should be sampled and analyzed separately on the sampling day of the two-week interval. Each batch sample should be composed of at least three grab samples collected at the start, mid-point, and end of the feed cycle to the batch.

5. Slug inputs of heavy metals to water pollution control plants should be eliminated to reduce sludge variability.

6. Plant staff should be encouraged to keep complete records of digested sludge analyses and process stream flows. Where lack of facilities or manpower prohibits routine analyses at the plant, samples should be sent regularly to a central laboratory

for analysis. Process control charts should be used to aid the operating staff in keeping the process "in control".

7. Improved digester mixing methods should be investigated. Residence time distribution studies should be used periodically to determine mixing efficiencies of digesters. To obtain a uniformly digested sludge product, plants should be encouraged to use control strategies (e.g., pH control, solids recycle, uniform pumping schedules) to optimize digester performance. Improvement of present metering devices such as raw sludge pumping meters and digester gas production meters should be investigated.

8. The ammonia gas electrode can be considered for use where regulations require monitoring of ammonia in sludges (and effluent).

9. Projects to expand on the work described above should include:

(a) a study of the dynamics and improved mixing in anaerobic digestion;

(b) investigations leading to improved methods of sludge withdrawal from anaerobic digesters where sludges are currently discharged batchwise;

(c) examination of sludge solids data from other pollution control plants to further characterize the processes during lengthy time periods (more than one year);

(d) an estimation of the costs of sampling and analyses;

(e) an investigation of the procedures used by operators of tank truck disposal units to regulate the rate of discharge of sludge from tank trucks, and procedures allowing WPCP superintendents to advise operators on optimum disposal rates; and

(f) an investigation of the consequences of solids fluctuations on chemical requirements at plants where sludges are dewatered.

1   INTRODUCTION

1.1   Scope of Report

    This report deals with sampling requirements to assess the physical-chemical quality of anaerobically digested sewage sludges. It is important to be aware of sources of variation to make sampling meaningful and efficient. Routine, but poorly understood, sampling methods may otherwise provide a large amount of data containing little useful information. Good sampling and complete data records reduce the effort necessary to obtain a maximum amount of information.

    With increased concern for sludge handling, treatment, and disposal, efficient sampling is required for sludge characterization. Previous studies (Chawla et al., 1974) have shown a marked variability in the physical-chemical content of digested sludges. Unfortunately, the variability could not be related to sampling procedures, nor attributed to any particular source of variation. Data were collected in this project to determine whether variations were systematic and attributable to some factor, or random variations due to inherent sludge heterogeneity. The data have been used to identify a baseline standard for efficient and practical sampling to permit sludge characterization with some degree of confidence. Familiar methods of data reduction (graphical time sequences, probability plots, averages, confidence limits, etc.) have been combined with more rigorous methods of data analysis (analysis of variance, time series analysis) to assist in data interpretation. This approach is required when randomness obscures systematic variations or trends which cannot be detected by visual inspection of the data. This is the situation for digested sludges.

    This study was performed (1974 to 1975) at five Ontario WPCP's operating under what were considered normal conditions. No changes were made in routine operating procedures at these plants, and no attempt was made to control the variations observed. The results are intended for modifying or substantiating existing sampling programs. Liquid sludges were sampled both at plants from which sludges were hauled to land disposal sites (batch mode) and at plants where sludges were dewatered (semi-continuous mode). Analyses included solids, nutrients (TKN, NH_3-N, phosphorus), and heavy metals (Fe, Al, Ni, Cu, Zn, Pb, Cd).

1.2   Relevance

Ever increasing volumes of digested sewage sludge are presenting treatment plant operators with the serious problem of sludge disposal. Burd (1968) felt that sludge handling and disposal were greatly neglected; while total sludge volume for a plant was frequently less than 1% of the total wastewater volume collected and treated, its handling and disposal often accounted for 25 to 50% of the total capital and operating cost of the treatment plant.

Anaerobic digestion of sewage sludge is used by many water pollution control plants in North America to reduce the volatile component of sludge solids to a stabilized, non-putrescible material. Digestion proceeds with a reduction in sludge volume and the production of methane gas, a useful by-product. Nevertheless, the volume of stabilized sludge remaining is large and a suitable method for its disposal must be selected.

Among the sludge disposal methods that have been considered are: lagooning; ocean disposal; sanitary landfill; underground injection; incineration; land disposal; and composting. Land disposal offers the greatest possibility for recycling nutrients back to the land.

Human wastes have been applied to land for hundreds or thousands of years as organic manures (Bates, 1972; Ewing and Dick, 1970). Law (1968) reviewed much of the work done in agricultural utilization of sewage sludge. Digested sewage sludge has a fertilizer value of 3.5 to 6.4% by weight of nitrogen, 0.8 to 3.9% by weight of phosphorus, and 0.2 to 0.7% by weight of potassium (Peterson et al., 1972). The value of digested sludge as a fertilizer is emphasized by the fact that 41% of the digested sludge produced in Ontario is spread onto farmers' fields (Black, 1975). Land disposal of sludge is feasible for the majority of Ontario sewage treatment plants which are relatively small; but together, the larger cities of Metropolitan Toronto, Hamilton, and London incinerate 41% of the sludge produced in Ontario (Black, 1975).

Despite the advantage of land disposal of digested sludge, there is concern over the buildup of substances including heavy metals, nutrients, and salts in the soil and groundwater. If applied in excess

of plant needs, ammonia in sludge can be converted by soil bacteria to nitrate. Contamination of groundwater by nitrate, which may move with downward percolating water, is then possible. Recent studies, however, have shown that considerable amounts (up to 60 to 75%) of ammonium-nitrogen in sludge applied to the land surface may be lost by volatilization, depending on soil environmental conditions and the rate at which sludge is applied (Beauchamp and Moyer, 1974; Ryan and Keeney, 1975).

Total dissolved solids and heavy metals in sufficient quantities can cause crop toxicity. Many studies have been conducted on potential toxic properties of heavy metals in crops, and on uptake of heavy metals by plants for human or animal consumption (Webber, 1972; Bates et al., 1974; Bradford et al., 1975; Mortvedt and Giordano, 1975; Bingham et al., 1975; Dowdy and Larson, 1975a; Sabey and Hart, 1975; Boswell, 1975; Dowdy and Larson, 1975b). Except in cases where sludge application on land is greatly in excess of safe levels, breakthrough of heavy metals to groundwater is not expected. At Celina, Ohio, after 10 years of sludge application to a clay loam soil, no appreciable buildup in the soil was noted for lead, cadmium, or copper; moderate increases were found for zinc and nickel. Chromium showed a great increase in the top 10 inches (25 cm), but deeper soil samples from 10 to 30 inches (25 to 76 cm) revealed that metal concentrations rapidly approached background levels found in a control field (Manson and Merritt, 1975).

Because heavy metals are likely to be a limiting factor in digested sludge application rates on land, metal concentrations in the sludge must be identified. Past analyses have shown that the metal concentrations in digested sludge vary considerably from one pollution control plant to another, and within the same plant over a period of time. Anderson (1956) noted a wide variation in concentrations of minor elements in digested sludge. This he attributed to the effect of different industrial and domestic sources. Sommers et al. (1973) found that heavy metal concentrations were highly variable between 10 Indiana treatment plant sludges with coefficients of variation ranging from 47% for iron to 152% for cadmium. In Ontario, Abbott (1971) found that heavy metal concentrations in digested sludge fluctuated greatly within

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a month and from month-to-month at different plants. He observed that metal levels in sludge reflected the industrial metal processing activity in the particular municipality. While this may be generally true for smaller Ontario towns, industry cannot be blamed completely for the presence of heavy metals in digested sludge. Klein et al. (1974) observed that, in New York City, residential areas without industry contributed from 25 to 49% of metals (including zinc, copper, and cadmium) in the total sewage flow, amounts frequently greater than contributions from the city's electroplating industries.

Examination of digested sludge using spectrochemical analysis (Gross, 1970) indicated that sample heterogeneity was a severe problem. The variability in the sample results was especially severe for Ba, K, P, Cr, Cu, Ni, and Pb, while variation between analyses performed at different times was not as critical. Van Loon et al. (1973) tested the reproducibility of the results of sludge analyses using atomic adsorption spectrophotometry, and also found that sample heterogeneity was a problem. It was recommended that several grab samples from a sludge digester be collected at the tank outlet and combined to form a "representative" sample. Chawla et al. (1974) examined digested sludges from four Ontario sewage treatment plants for 15 months. They observed that the variability of heavy metals in all the sludges was great with relative standard deviations of about 30 to 50% of the mean concentrations. The magnitude of the digested sludge variability in North America is similar in countries such as Britain (Berrow and Webber, 1972) and Sweden (Oden et al., 1970). The variabilities observed in these studies prompted the intensive sampling methodology development of this project.

In addition to sample heterogeneity, methods of laboratory analysis might cause some variation. A group of ten Ontario laboratories analyzed three, air-dried, ground, digested sludge samples. A review of their unpublished results revealed that the elements with the greatest variability (20% relative standard deviation, RSD) were Ni, Cd, Cr, and Al. The results for Zn, Cu, Pb, and Mn were less variable with RSD's from 4 to 16%.

Although the potential for land disposal of digested sludge is great, sludge must be applied at rates that prevent excessive buildup of heavy metals, ammonia, and salts in soil. Application rates which are stipulated imply that the concentrations of these substances have been quantified. This report deals with the estimation of the number of samples required to predict digested sludge constituent concentrations with a given degree of confidence.

2   OBJECTIVES

The objectives of this project were:

1. to identify and compare the source(s) of constituent variability in anaerobically digested sludges by determining whether observed variations arose from sample handling and analytical measurements, from changes in the composition with time, or from inherent heterogeneity;

2. to determine the number of samples and the sampling frequency required to estimate constituent concentrations in digested sludge with a given degree of precision;

3. to determine the hydraulic mixing efficiencies of anaerobic digesters; and

4. to evaluate an ammonia gas sensing electrode for measuring the NH_3-N concentration in digested sludge.

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3   PROCEDURES

3.1   Selection of Plants

A selection of water pollution control plants was made from predominantly agricultural areas of Southwestern Ontario. Five sewage treatment plants were studied intensively; their major characteristics are given in Table 1. The activated sludge process was used at all the plants with anaerobic digestion of raw and waste activated sludges.

The plants selected were typical examples of plants practising land disposal of digested sewage sludges. No sampling was carried out at treatment plants serving large industrial cities, because economic considerations may make land disposal of their sludge prohibitive. Four plants used two-stage anaerobic digestion of sludge, while one (Milton WPCP) had single-stage digestion. Organic loading rates (Table 2) indicated that the digestion processes were low rate (0.04 to 0.10 lb $VS \cdot ft^3 \cdot day^{-1}$) though the loadings varied over a broad range. Other operating data (Tables 2 and 3) indicated that the systems were operating within acceptable limits. Two plants (Simcoe and Chatham) dewatered the secondary digested sludge using centrifuges, which allowed systematic sampling of a large portion of the digester contents. At Milton, Oakville S.E. (South East), and at Tillsonburg, liquid sludge was hauled by truck; this practice permitted observation of the variability in sludge discharged from a digester in separate batches.

With the exceptions of the Milton and Oakville S.E. plants, the digested sludges contained phosphorus removing chemicals. Lime sludge from the secondary clarifier at the Milton plant was treated separately from the raw primary clarified sludge; the Oakville S.E. plant had not yet (June, 1975) installed phosphorus removal facilities.

3.2   Sampling Designs

3.2.1   Description of sampling designs

Sampling designs used to achieve the objectives of this study were adapted from techniques used in the chemical industry (Davies, 1956; Davies and Goldsmith, 1972), in agriculture (Snedecor and Cochran, 1967), and in the marine sediment sampling field (Kelly and McManus, 1969).

TABLE 1. CHARACTERISTICS OF WATER POLLUTION CONTROL PLANTS

WPCP	Population of Community	Raw Sewage Flow		Phosphorus Removal Chemical	Sludge Dewatering Device	Sludge Disposal Method
		(MIGD)	($m^3 \cdot day^{-1}$)			
Simcoe	11,000	2.0	9,090	$FeCl_3$**	Centrifuge	Cake disposed of on plant site.
Chatham	34,400	4.5	20,500	$FeSO_4$	Centrifuge	Cake disposed of on plant site; some cake used on farm fields. Liquid sludge trucked to farm fields.
Milton	7,700	0.80	3,630	Lime	-	Liquid sludge trucked to farm fields.
Oakville S.E.	16,000*	1.6	7,260	-	-	Liquid sludge trucked to farm fields.
Tillsonburg	6,400	0.66	3,000	Alum	-	Liquid sludge trucked to farm fields.

* Population estimated on basis of 100 Igal$\cdot$day$^{-1}\cdot$Capita^{-1}.
** Later changed to $FeSO_4$.

TABLE 2. PRIMARY DIGESTER OPERATING PARAMETERS

WPCP	Volatile Acids	Total Alkalinity	pH	Temperature		Organic Loading Rate		Average Gas Production			
	$mg\ HOAc \cdot l^{-1}$	$mg\ CaCO_3 \cdot l^{-1}$		°F	°C	$lb\ VS \cdot ft^{-3} \cdot day^{-1}$	$kg\ VS \cdot m^{-3} \cdot day^{-1}$	$ft^3 \cdot day^{-1}$	$m^3 \cdot day^{-1}$	$ft^3 \cdot lb^{-1}\ VS\ added$	$m^3 \cdot kg^{-1}\ VS\ added$
Simcoe	120	4,800	7.6	93	34	0.0318*	0.510	**	**	**	**
Chatham	270	1,590	7.1	92	33	0.0924	1.48	48,800	1,380	6.92	0.432
Milton	96	1,340	7.4	97	36	0.0698	1.12	***	***	***	***
Oakville S.E.	170	2,940	7.3	93	34	0.0120	0.192	14,000	396	19.8	1.24
Tillsonburg	110	2,220	7.0	95	35	u.0116	0.186	**	**	**	**

* Estimated from 1973 MOE and Simcoe WPCP records.
** No meter.
*** Meter not working.

TABLE 3. RAW AND DIGESTED SLUDGE CHARACTERISTICS*¹

WPCP	Raw Sludge				Digested Sludge			
	Pumping Rate		Total Solids Concentration	Volatile Solids Concentration	Withdrawal Rate		Total Solids Concentration	Volatile Solids Concentration
	$Igal \cdot week^{-1}$	$m^3 \cdot week^{-1}$	% wt.	% wt.	$Igal \cdot week^{-1}$	$m^3 \cdot week^{-1}$	% wt.	% wt.
Simcoe	51,100	232	2.69*²	1.89*³	41,000	186	3.23	1.52
Chatham	245,000	1,110	4.30	2.19	203,000	923	3.92	1.45
Milton	70,100	318	2.61	1.85	52,200	237	1.22	0.59
Oakville S.E.	28,000	127	2.75	1.79	22,600*⁴	103	3.49	1.78
Tillsonburg	33,500	152	3.50	2.28	13,200	60	4.17	2.17

*¹ Except where noted, total and volatile solids concentrations were averages measured during the sampling programs.
*² From MOE 1974 records.
*³ From MOE 1973 records.
*⁴ Withdrawn at irregular intervals. Rate estimated from data for period July to September, 1975.

Similar approaches have been adopted in effluent sampling surveys in Great Britain (Montgomery and Hart, 1974). The technique used is called Analysis of Variance (ANOVA); it is useful when observations may be affected by a number of influencing sources. Analysis of the observations for each constituent at each sampling site permitted a separation of the components of variance attributable to:

1. sample retrieval, testing (physical and chemical), and all unaccountable sources of variation;
2. variations in a discrete batch of sludge discharged to a tank truck;
3. variations in the feed to a dewatering device at plants where sludge was dewatered;
4. batch-to-batch variations at plants where liquid sludge was hauled by tank truck;
5. day-to-day variations at plants where sludge was dewatered, and at plants where sludge was hauled by tank truck; and
6. week-to-week variations at the Chatham WPCP.

Constituents measured included: total solids, volatile solids, total dissolved solids, pH, nutrients, and heavy metals.

The components of variance are of interest because, once isolated and estimated, they show which sources contribute the most (or least) variability to the overall system. An example of the calculations in the ANOVA for an unbalanced sampling design is given in Section I-1, Appendix I.

Once the components of variance have been estimated, they may be used to establish the optimum sampling strategy to detect changes in the sludge based on the original sampling plan employed. This procedure is called 'optimum allocation of sampling resources', and is described in Section I-2, Appendix I. Sampling expenses in the form of cost ratios are formulated within the allocation procedure. These ratios identify, for example, the cost of analysis of a sample compared to the cost of physically taking the sample. Another cost ratio might be the cost of sampling many times within one day to the cost of sampling only once or twice daily but on many different days. Estimation of cost ratios for the purposes of this report is included in Appendix I.

In other situations in which sample size determinations have been necessary, the required sample size has been estimated using a relationship between the allowable error in the sample mean and the relative standard deviation (RSD) of the mean (e.g., Klee and Carruth, 1970; Snedecor and Cochran, 1967; Petersen and Calvin, 1965). The RSD is a measure of the variability of the observations, and this widely applied technique of sample size determination is described more completely in Section 1-3, Appendix I. While this method does indicate the total number of samples needed, it does not indicate the most efficient sampling arrangement. The advantage of separating the components of variance and of using the procedure for optimum allocation of sampling resources is that the sampling distribution required to efficiently estimate mean parameter concentrations is revealed. Components of variance were estimated for the five plants monitored in this study in what have been called short term sampling surveys for the purposes of this report. Descriptions of these short term surveys are given for each WPCP in the following sections.

In addition to the short term sampling surveys carried out at the five plants, examinations of long term records from two WPCP's were conducted. Records of total and volatile solids concentrations in primary clarified raw sludge and secondary digested sludge from the Tillsonburg WPCP were examined for the period January 1974 to November 1975. Weekly mean concentrations were evaluated to detect periodicities or autocorrelations among the sequence of observations, and to determine the extent of variability over this time period. The method of time series analysis was used for this (Box and Jenkins, 1970). This method can indicate the interdependence amongst a series of observations. The second study, at the Chatham, Ontario WPCP, consisted of two parts. Firstly, an evaluation was made of raw and digested sludge solids records similar to those at Tillsonburg. The records extended from July 1973 to December 1975. The second part consisted of daily measurements of NH_3-N, TKN, total and volatile solids, nickel, copper, zinc, and lead concentrations from June 23 to November 14, 1975. The second part gave an indication of chemical variability of digested sludge during a period of time sufficient to show trends not evident in a short sampling period.

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The presence of significant trends may be readily confirmed by non-parametric statistical methods (Kendall, 1970).

3.2.2   Simcoe WPCP

At the Simcoe WPCP, each digester in the two-stage system has a capacity of 270,000 Igal (1,230 m³). Data concerning the raw primary clarified and secondary digested sludges are given in Table 3. Raw sludge and scum were pumped to the primary digester seven days per week at an average rate of 51,100 Igal·week⁻¹ (232 m³·week⁻¹). Digesting sludge was transferred batchwise from the primary to the secondary digester twice a week. A centrifuge was used to process about 41,000 Igal·week⁻¹ (186 m³·week⁻¹) of digested sludge at the time of the study. Digester supernatant was not returned to the plant from the secondary digester, though centrate was.

Triplicate grab samples were collected six times daily at intervals of one hour from the conduit feeding the centrifuge for a total of 18 grab samples per day (six samples times three repeats per sample). A daily composite sludge sample, using a siphon tank arrangement described by Hodges (1959), was also collected in this period. The tank was continuously mixed, and a composite sample was collected at the end of a daily run. Eleven continuous working days from August 19 to September 3, 1974 were included in this study before a plant upset forced termination of sampling.

Five sets of 'diagnostic checks' from the Simcoe plant were examined in a period from December 1974 to February 1975, about three months after the original survey. Five non-replicated samples were collected during the same two-hour interval on each of five different days to determine whether the chemical composition of the digested sludge had changed since the short term sampling period several months earlier.

3.2.3   Chatham WPCP

The Chatham WPCP has a two-stage sludge digestion system and a centrifuge for sludge dewatering. The primary digester has a capacity

of 530,000 lgal (2,410 m^3). Raw primary clarified sludge is pumped on a near-continuous basis to the primary digester; primary digested sludge is transferred to the secondary digester on a semi-continuous basis of seven minutes of pumping per hour. This transfer rate corresponds to about 198,000 lgal·week^{-1} (900 m^3·week^{-1}). The contents of the secondary digester were mixed for approximately four hours to redistribute the sludge blanket at the completion of each centrifugation period. An undetermined volume of supernatant was recycled to the aeration tank from the secondary digester on weekends. Sludge characteristics are given in Tables 2 and 3.

Triplicate grab samples were collected five times daily at intervals of 90 minutes from March 3 to March 21, 1975 during normal weekday shifts. The 15 daily samples (i.e., three repeats per sample times five samples) were collected during 15 consecutive days of centrifuge operation for a grand total of 225 samples in the study. The sludge samples were collected from a conduit in the basement of the digester building where the sludge was withdrawn from digester sumps to feed the centrifuge.

A subsequent long term study extending from June to November, 1975 served as a supplementary diagnostic check of the short term sampling program at the Chatham plant. Three grab samples were composited for analysis on each day of centrifuge operation. Samples were collected at the beginning, mid-point, and end of a centrifuge run in accordance with the findings of the short term survey.

3.2.4   Milton WPCP

The Milton WPCP uses a single-stage digester having a volume of 165,000 lgal (751 m^3). A holding tank for the digested sludge (estimated capacity 81,400 lgal, 370 m^3) follows the digester. Characteristics of the digestion process at this WPCP are summarized in Tables 2 and 3. Raw primary clarified sludge and scum were pumped twice daily from each of two scum pits. Raw sludge was pumped to the digester at a rate of 70,100 lgal·week^{-1} (318 m^3·week^{-1}). About 52,300 lgal (238 m^3)

of digested sludge were removed by tank truck each week. Digester supernatant was returned to the plant on an infrequent basis.

Feed to each batch truckload of sludge was sampled three different times during loading. Collection was made at the start, mid-point, and end of each pumping cycle to each truckload. Samples were randomly replicated to reduce the total sample size. In total, 62 batches of digester sludge were sampled during 25 separate days between June 23 and July 31, 1975, yielding a grand total of 254 individual samples. There were 68 pairs of replicate samples. This sampling program produced an unbalanced ANOVA; consequently, calculations for unequal sample sizes were used. These are discussed in Appendix I with an example of the sampling design.

On each sampling day, either two or three batches of sludge representing 24 or 25 yd^3 (18 or 19 m^3) were hauled away depending on the tank truck capacity. The trucks generally took 30 minutes to fill with sludge, so the interval between samples was 10 to 15 minutes within one load. Combining the time required for a round trip to the disposal site with the time for loading and emptying the truck, the time for one sampling cycle was slightly greater than one hour. The digested sludge was collected from a pipe leading to the tank truck from the sludge holding tank.

3.2.5   Oakville S.E. WPCP

Two-stage anaerobic digestion of sludge is used at the Oakville S.E. plant. Operating parameters for the primary digester (Table 2) are within the range considered satisfactory for digestion. The average solids concentrations in raw and digested sludges at the plant are presented in Table 3. Each digester has a capacity of 365,000 Igal (1,660 m^3). Each day, 4,000 Igal (18.2 m^3) of raw primary clarified sludge were pumped to the primary digester. The raw sludge displaced sludge from the bottom of the primary digester to the secondary digester. Digested sludge was hauled intermittently from the plant, depending on weather conditions and the availability of a tank truck. On hauling days, a maximum of five loads of 5,700 Igal (25.9 m^3) each were discharged from the secondary digester.

The volume of supernatant returned to the plant from the secondary digester is dependent upon the volume of digested sludge removed by tank trucks and upon the volume of primary clarified raw sludge pumped daily to the primary digester. When both digesters are operating near capacity, raw sludge pumping to the primary digester causes a displacement of primary digested sludge to the secondary digester, resulting in a discharge of a corresponding amount of supernatant. This amounted to about 4,000 gallons of supernatant (18.2 m^3) per day.

The sampling design at the Oakville S.E. WPCP was essentially the same as that used at the Milton WPCP. Three separate samples, randomly replicated, were drawn from sludge pumped to each of 33 batch truckloads. These batches were hauled away on eight days between July 16 and September 10, 1975. Included in the program were 48 pairs of replicate samples. Time for loading the truck varied between 14 and 20 minutes, depending on the sludge solids concentration; the time interval between samples was about 7 to 8 minutes. One sampling cycle, including the time to reach the disposal site, to spread the sludge and to return, was 60 to 75 minutes. Digested sludge samples were obtained from the truck loading line at a sampling sink in the basement of the digester building.

3.2.6   Tillsonburg WPCP

Both digesters in the two-stage system have a capacity of 224,000 Igal (1,020 m^3). Operating parameters for the primary digester are presented in Tables 2 and 3. Raw sludge and scum were pumped daily to the primary digester at an average rate of 33,500 Igal·week^{-1} (152 m^3·week^{-1}). Primary digested sludge was transferred to the secondary digester by means of an overflow box during pumping of raw sludge to the primary digester. Each week 20,200 Igal (91.8 m^3) were removed from the secondary digester by tank trucks.

The Tillsonburg plant was the first plant at which batch loads were examined. Two loads of sludge were removed on each of two days every week. In October 1974, four batch loads were sampled, corresponding

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to four separate haulage days within a two-week interval. The second of the two loads was always tested. Ten individual samples were systematically collected from the tank truck outlet at the disposal site on each occasion, giving a grand total of 40 samples. This sampling program allowed a thorough examination of the tank truck contents after loading and transit to a disposal site.

3.3   Residence Time Distribution Studies

Residence time distribution (RTD) studies were conducted for the digesters at Simcoe and Chatham. The variability of sludge discharged from a digester is influenced by the degree of mixing within the tank. Moderate variations in inert feed materials are expected to be damped out significantly by the characteristically long residence times encountered in digestion systems. Loffell (1955) used radioactive phosphorus (^{32}P) to study mixing in digesters, and found that natural mixing was inadequate for good digestion. Sodium fluoride, proposed by Tenney and Budzin (1972) and Verhoff et al. (1974) as a tracer, was used in the digester RTD studies conducted in this project.

The data from RTD studies can be interpreted by different models. Tenney and Budzin (1972) included deadwater regions in their studies, but did not include bypass flow or short circuiting effects. A mixed model incorporating deadwater regions and bypass flow as suggested by Cholette and Cloutier (1959) or Levenspiel (1972) appears to better satisfy the characteristic washout curves for at least one of the digesters tested in this study. The mixed model has previously been used to describe flow through real stirred-tank reactors, and might be expected to apply to large tanks such as digesters.

For the first RTD study at the Simcoe WPCP, 71 lb (32 kg) of sodium fluoride dissolved in tap water were injected into the secondary digester in a pulse fashion. A fluoride ion selective electrode (Orion Research, 1973) was used to measure the fluoride ion in the feed to the centrifuge. The electrode was connected to a millivoltmeter and a strip-chart recorder. The background fluoride concentration was $1 \text{ mg} \cdot l^{-1}$.

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In the second RTD study, 100 lb (45.4 kg) of sodium fluoride were injected into the primary digester in a pulse fashion. Primary digested sludge samples were collected at the sludge transfer pump when sludge was transferred between the digesters, usually twice a week. Samples were collected during the transfer period at 20 minute intervals, corresponding to volumes of about 2,000 Igal (9.1 m^3).

Residence time distribution studies were also carried out on both digesters at the Chatham WPCP. The RTD study of the primary digester was initiated by pumping 300 lb (136 kg) of sodium fluoride dissolved in tap water into the digester from the scum pit during a three-hour period. This was considered to be a pulse input when compared to the much longer hydraulic residence time. Five samples of primary digested sludge were collected and analyzed for fluoride during centrifuge operations at three-hour intervals each day on 17 consecutive days.

For the RTD study of the secondary digester, 220 lb (100 kg) of sodium fluoride were added to the digester during a two-hour interval. Seven daily centrifuge feed samples were collected at intervals of 90 minutes from March 3 to March 21, 1975 throughout centrifuge operations. From March 24 to April 4, 1975, three samples were collected on weekdays at four-hour intervals.

3.4   Analytical Methods

Nutrient and heavy metal analyses were performed using methods specified in the Analytical Methods Manual (Laboratory Services Section, Wastewater Technology Centre, 1976). More specifically, NH_3-N, TKN, and total phosphorus were determined by automated techniques; total organic carbon analyses were carried out with a Beckman Model 915 TOC analyzer; heavy metal analyses were performed by atomic absorption techniques.

Total solids, volatile solids, total dissolved solids, and pH were analyzed according to Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WPCF, 1971). Total alkalinity and volatile acids were analyzed using the procedure described by DiLallo and Albertson (1961).

3.4.1 Fluoride determination by selective ion electrode

With some modification, the procedure used to determine fluoride concentration in sludge using a specific ion electrode is described in the operating manual for this instrument (Orion Research, 1973). To overcome the effect of phosphorus removal chemicals in the sludge, particularly ferrous sulphate, on the recovery of fluoride ion, certain alterations were made to the technique. A total ionic strength adjustment buffer (TISAB) solution was prepared following the procedure described by McQuaker (1973), but sodium citrate concentration was increased to 30 $g \cdot l^{-1}$ from 12 $g \cdot l^{-1}$. In addition, concentrated H_2SO_4 was slowly added to reduce the sludge sample pH to 2. Twenty-five millilitres of TISAB solution were added to 25 ml of the pH adjusted sample. The pH was then readjusted to a value of 5.3 with 10 N NaOH, and the fluoride concentration was measured using the known addition technique described in the manual.

3.4.2 Ammonia determination by gas sensing electrode

Because ammonia has been identified as a critical factor in sludge application to land, it is desirable to measure its concentration in sludge at the plant site. The ammonia gas sensing electrode (Orion Research, 1974) was evaluated for field use for NH_3 measurement in digested sludge. This appears to be a novel application for field use of the electrode. Previous work with the electrode has been limited to laboratory examinations of ammonia concentrations in seawater, river water, and domestic and industrial wastewater (Thomas and Booth, 1973; LeBlanc and Sliwinski, 1973; Kennewell and Long, 1974).

The initial phase of the study was designed to evaluate the effect of different sample preparation techniques on the ammonia concentration measured, and to compare the measurement of NH_3-N in digested sludge using the electrode method and an automated colourimetric method. Sludge from the Simcoe WPCP was used in these experiments.

Two electrode measurement techniques described in detail by the manufacturer were evaluated - the calibration technique and the known addition technique. The calibration technique is a procedure in

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which known standards are used to calibrate the output of the measuring device, in this case a millivoltmeter. The ammonia concentration in digested sludge varied from approximately 10^{-2} to 10^{-1} M. However, each sample was diluted by a factor of 10 to reduce the total dissolved solids concentration and to improve sample mixing effectiveness. A calibration curve was constructed using ammonium chloride standards over the range 10^{-4} to 10^{-1} M. Distilled water was used for the preparation of standards and dilutions. The method of known addition was also used. This consisted of measuring the electrode potential in a diluted sample, spiking the sample with a known standard solution, and remeasuring the newly developed potential. Change in potential was related to the original ammonia concentration of the sample. Detailed instructions are available in the electrode reference manual (Orion Research, 1974).

Because a filtered sample is required for analysis by the automated colourimetric procedure, the electrode was also evaluated with filtered and unfiltered diluted sludge samples. Success of the non-filtered analyses would eliminate the necessity of sludge filtration which is very time consuming. Therefore, three sample preparation procedures were evaluated:

1. dilution without filtration;
2. dilution followed by filtration: the diluted sample was passed through a glass fibre filter (Reeve Angel 934AH) prior to filtration through a 0.45 μ pore size membrane filter (Gelman, Metricel GA-6); and
3. filtration followed by dilution: the sample was centrifuged prior to filtration firstly through a glass fibre and then membrane filter.

Four replications were run for each preparation. The last two replications were performed three days after the first two; this time lapse was included as a factor in the analysis and interpretation of the results.

In addition to electrode analysis using the calibration and known addition techniques, a total of eight of the filtered samples were submitted for routine analysis by the automated technique. The concentrations assessed by all methods were evaluated.

After the initial experimental stage described above, the staff of the Chatham WPCP were provided with an electrode to permit evaluation of the instrument in the field. The known addition technique with diluted, unfiltered samples was chosen as the basis for comparison with the diluted, filtered samples analyzed using the automated colourimetric technique. Filtration and automated analyses were performed at the Wastewater Technology Centre. A total of 45 samples collected between June 23 and August 29, 1975 were analyzed using both methods.

4 OBSERVATIONS AND DISCUSSION

For brevity, discussion of the ANOVA results for the short term sampling surveys performed at each plant has been limited to four important parameters: NH_3-N, TKN, total solids, and zinc. A statistical summary for these parameters is presented in Table 4. Other heavy metals varied in patterns similar to those for zinc and, therefore, have not been discussed in detail to avoid repetition; total dissolved solids, being distributed in the liquid phase, behaved much the same as ammonia concentration; volatile solids and total organic carbon resembled variations in total solids. A summary for these other parameters is presented in Appendix II; probability distributions for raw data are presented in Appendix III.

4.1 Simcoe WPCP

Mean parameter concentrations between days and mean concentrations between samples within days in Simcoe digested sludge are shown in Figures 1 and 2, respectively. The daily sequence indicated that ammonia was the least variable of the four parameters. No major trends were observed during the 11 sampling days. A significant decline in concentrations was observed, however, in the sequence of samples within a day (Figure 2). The decline was more evident for TKN, total solids, and zinc than for ammonia.

Significant differences between days and between samples within days were detected by the ANOVA (Table 5) for all parameters. Separation of the components of variance, s^2, indicated that variations between samples within days provided the greatest contribution to sludge variability. Variations between days and between repeats within hourly samples did not contribute to the variance to the same extent as the within day factor.

Sampling requirements based on the optimum allocation of resources are listed in Table 6. The requirements for each parameter were different owing to the varying magnitudes in the components of variance.

TABLE 4.   STATISTICAL SUMMARY OF PARAMETERS IN DIGESTED SLUDGES

| WPCP	Parameter	Grand Mean mg·l^{-1}	Sample Standard Deviation mg·l^{-1}	RSD Wet wt. basis %	95% CL of Mean mg·l^{-1}	Range of Parameter mg·l^{-1}	RSD Dry wt. basis %
Simcoe	TKN	2,900	226	7.82	31	2,440 - 4,110	8.87
	NH$_3$-N	1,370	75.3	5.50	11	970 - 1,530	11.4
	Total Solids	32,300	3,500	10.8	490	25,800 - 45,400	-
	Zn	81.2	8.75	10.8	1.2	60.4 - 114	9.88
Chatham	TKN	1,710	374	21.8	49	1,040 - 2,980	16.2
	NH$_3$-N	543	66.1	12.2	9	420 - 660	14.5
	Total Solids	39,500	6,030	15.3	790	26,800 - 50,700	-
	Zn	71.5	12.2	17.1	1.6	46.0 - 114	11.0
Milton	TKN	829	403	48.7	58	120 - 2,230	73.7
	NH$_3$-N	311	73.3	23.5	11	112 - 526	102
	Total Solids	12,200	8,630	70.9	1,250	1,230 - 36,800	-
	Zn	10.9	8.74	80.4	1.3	0.25 - 36.0	38.2
Oakville S.E.	TKN	2,540	637	25.1	125	1,020 - 3,740	37.0
	NH$_3$-N	913	74.2	8.13	12	620 - 1,040	72.2
	Total Solids	34,900	14,100	40.4	2,300	6,700 - 86,500	-
	Zn	32.1	14.7	45.6	3.0	4.90 - 96.0	12.6
Tillsonburg	TKN	2,320	405	17.5	130	1,040 - 2,880	18.0
	NH$_3$-N	567	15.3	2.70	5	530 - 600	6.38
	Total Solids	41,700	3,020	7.24	970	36,900 - 46,000	-
	Zn	55.6	2.72	4.89	0.9	50.8 - 59.6	2.82

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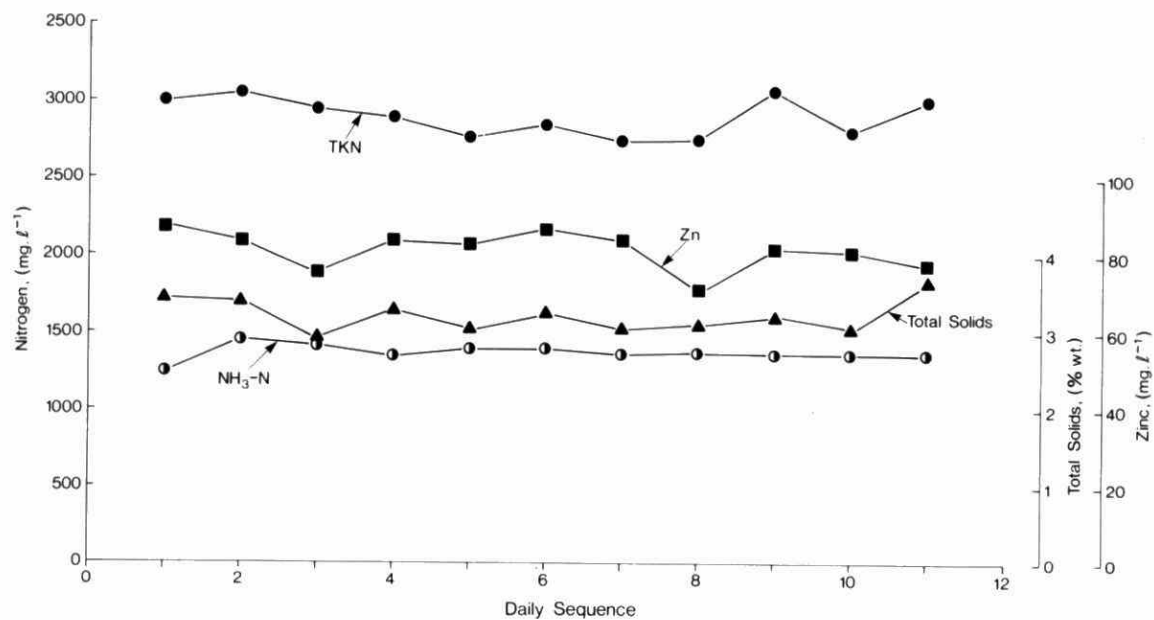
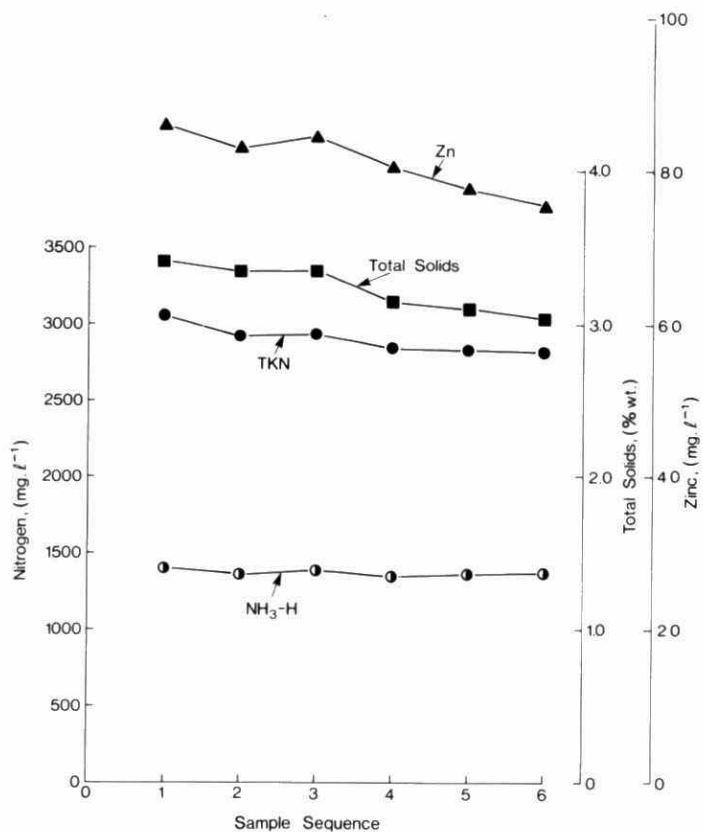FIGURE 1. MEAN PARAMETER CONCENTRATIONS BETWEEN DAYS, SIMCOE WPCP

FIGURE 2. MEAN PARAMETER CONCENTRATIONS BETWEEN SAMPLES
WITHIN DAYS, SIMCOE WPCP

TABLE 5. ANALYSIS OF VARIANCE, SIMCOE SLUDGE

Source of Variation	df	Total Solids			TKN		
		Mean Square	Significance	$s^2(\%)^2$	Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$
Between days	10	8.3568639	**	0.03272901	273,884	**	10,946
Between samples within days	55	2.4656427	**	0.07671538	76,850	**	17,891
Between repeats within samples	132	0.1641813		0.01641813	23,176		23,176

Source of Variation	df	NH_3-N			Zinc		
		Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$	Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$
Between days	10	42,068	**	1,891	396.8	*	13.2
Between samples within days	55	8,040	**	2,268	158.9	**	47.0
Between repeats within samples	132	1,237		1,237	18.0		18.0

* Significant at 95% level.
** Significant at 99% level.

TABLE 6. OPTIMUM ALLOCATION OF SAMPLING RESOURCES: NUMBER OF SAMPLES AND SAMPLING DISTRIBUTRION FOR STIPULATED PRECISIONS

		NH$_3$-N			TKN			Total Solids			Zinc		
		$\pm10\%\bar{x}$	$\pm25\%\bar{x}$	$\pm50\%\bar{x}$	$\pm10\%\bar{x}$	$\pm25\%\bar{x}$	$\pm50\%\bar{x}$	$\pm10\%\bar{x}$	$\pm25\%\bar{x}$	$\pm50\%\bar{x}$	$\pm10\%\bar{x}$	$\pm25\%\bar{x}$	$\pm50\%\bar{x}$
Simcoe	No. of days	1	1	1	3	1	1	3	1	1	2	1	1
	No. of samples/day	1	1	1	1	1	1	2	1	1	3	1	1
	TOTAL	1	1	1	3	1	1	6	1	1	6	1	1
Chatham	No. of weeks	1	1	1	23	4	1	6	1	1	9	1	1
	No. of days/week	1	1	1	1	1	1	1	1	1	1	1	1
	No. of samples/day	2	1	1	1	1	1	2	2	1	2	2	2
	TOTAL	2	1	1	23	4	1	12	2	1	18	2	1
Milton	No. of days	23	4	1	1	1	1	1	1	1	28	4	1
	No. of batches/day	1	1	1	107	17	4	199	32	4	10	10	10
	No. of samples/batch	1	1	1	1	1	1	1	1	1	1	1	1
	TOTAL	23	4	1	107	17	4	199	32	4	280	40	10
Oakville S.E.	No. of days	1	1	1	7	1	1	1	1	1	1	1	1
	No. of batches/day	3	1	1	4	4	1	86	14	3	93	15	4
	No. of samples/batch	1	1	1	1	1	1	1	1	1	1	1	1
	TOTAL	3	1	1	28	4	1	86	14	3	93	15	4
Tillsonburg	No. of batches	1	1	1	8	1	1	3	1	1	1	1	1
	No. of samples/batch	1	1	1	2	2	1	1	1	1	1	1	1
	TOTAL	1	1	1	16	2	1	3	1	1	1	1	1

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During the sampling program at the Simcoe WPCP, a composite sample was collected daily for comparison with grab samples. Means and variances of composite and grab sample parameters were compared, and no significant differences were found at the 95% confidence level. Because there were no significant differences, the composite samples were not used in further studies.

Three months after the original sampling survey, a series of check samples were collected on five different occasions. The five samples were collected during a period from December 1974 to February 1975. Each of the five samples consisted of a composite to account for the variations previously observed within a day. The mean value for several parameters in each diagnostic check, together with mean parameter concentrations from the more intensive study, are presented in Table 7. The checks indicated that major changes had occurred in the characteristics of the sludge, including:

1. a decrease in parameter concentrations in the liquid phase: average NH_3-N concentration decreased from 1,370 $mg \cdot l^{-1}$ to as low as 873 $mg \cdot l^{-1}$, average total dissolved solids concentration decreased from 1,520 $mg \cdot l^{-1}$ in the first study to as low as 1,010 $mg \cdot l^{-1}$ in the diagnostic checks;

2. a major increase in most parameter concentrations in two of the five diagnostic checks: the increases were associated with an approximate doubling of the total solids concentration when compared to results of the initial study; and

3. on a dry weight basis, three checks revealed that: iron and aluminum had decreased from levels in the original study, nickel, copper, and cadmium were approximately unchanged, and zinc and lead had increased from values observed in the intensive study.

The diagnostic checks showed that significant concentration changes two to three months after a sampling survey may be expected. Major changes occurred even within the series of diagnostic checks

during a period of only one to two weeks. Because the sampling was as carefully controlled during the checks as during the original sampling period, the change in parameter concentrations can be construed primarily as within plant variability.

TABLE 7. MEAN PARAMETER CONCENTRATIONS OBSERVED IN CHECKS OF SIMCOE DIGESTED SLUDGE*

Parameter	Short Term Sampling Survey		Diagnostic Checks**				
	Mean**	±95% CL	1	2	3	4	5
TKN	2,900	2,870-2,930	2,560	4,010	3,580	2,430	2,450
NH$_3$-N	1,370	1,360-1,380	873	995	1,050	933	1,020
Total P	411	391-431	426	1,150	530	234	386
TOC	6,640	6,540-6,740	5,690	13,200	13,100	6,280	5,710
Total Solids	32,300	31,800-32,800	26,700	72,300	69,500	29,500	30,200
Volatile Solids	15,300	15,100-15,500	13,200	30,300	28,700	13,800	14,600
Total Dissolved Solids	1,520	1,480-1,560	1,010	1,010	1,080	1,060	1,140
pH	7.54	7.52-7.56	7.52	7.48	7.58	7.54	7.54
Fe	3,880	3,800-3,960	2,060	6,350	6,690	2,670	2,620
Al	142	139-145	130	325	287	116	116
Ni	1.1	1.1-1.2	1.1	2.8	2.6	1.2	1.4
Cu	18.8	18.5-19.1	15.9	39.9	39.9	18.9	19.4
Zn	81.2	80.0-82.4	57.3	167	175	88.2	97.6
Pb	14.6	14.3-14.9	18.2	50.1	51.0	24.6	27.4
Cd	2.5	2.5-2.6	2.4	6.0	5.6	2.7	2.8

* Diagnostic checks were sampling surveys on five different days.
** All results in mg·l^{-1}except pH.

4.2   Chatham WPCP

Mean parameter concentrations between days within weeks, between samples within days, and between weeks are presented in Figures 3, 4, and 5, respectively. A statistical summary of the four parameters is given in Table 4. Ammonia was observed to be the most constant parameter within a day; TKN, total solids, and zinc all decreased in concentration within a day. Within a week, ammonia was again the least variable, while TKN and total solids decreased in concentration. Zinc exhibited a marked increase on the fifth day of a week, but was otherwise constant between days. Significant increases in mean weekly concentrations were observed for all four parameters in digested sludge at Chatham (Figure 5).

From the ANOVA (Table 8), highly significant differences were measured between samples within a day for all parameters. TKN, ammonia, and zinc also exhibited highly significant differences between weekly periods. TKN displayed highly significant differences between days within a week, while ammonia and zinc varied less significantly between days.

With respect to the components of variance, differences between samples within a day and between weeks contributed the most to overall variability (Table 8). The largest component of variance for the nitrogen (TKN and NH_3-N) parameters was the between weeks factor; conversely, the largest component of variance for total solids and zinc was the between samples within days factor. Contributions to variability from repeats within a sample and from days within a week were smaller except in one case. The optimum sampling arrangement derived from the components of variance is presented in Table 6.

4.3   Milton WPCP

Statistical data for TKN, ammonia, total solids, and zinc in digested sludge from Milton were presented in Table 4. An unbalanced design was used for the ANOVA (Table 9) as the number of batch truck loads varied from day-to-day, and because random replications of samples within batch loads were introduced to reduce the total sample size. A description and example of the ANOVA are presented in Appendix I.

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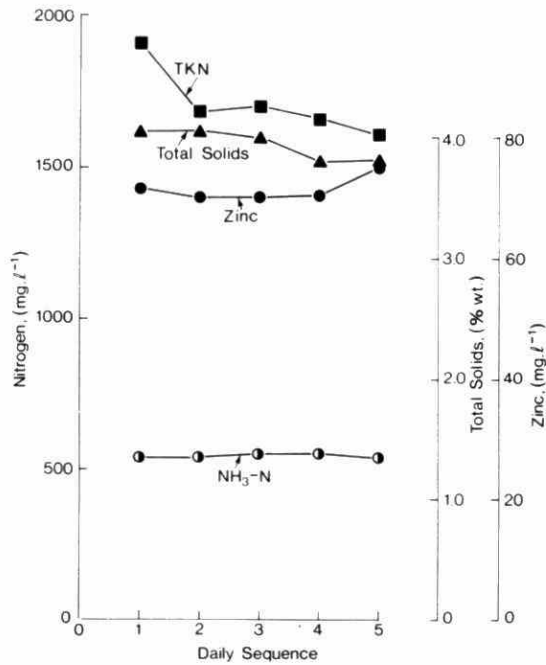
FIGURE 3. MEAN PARAMETER CONCENTRATIONS BETWEEN
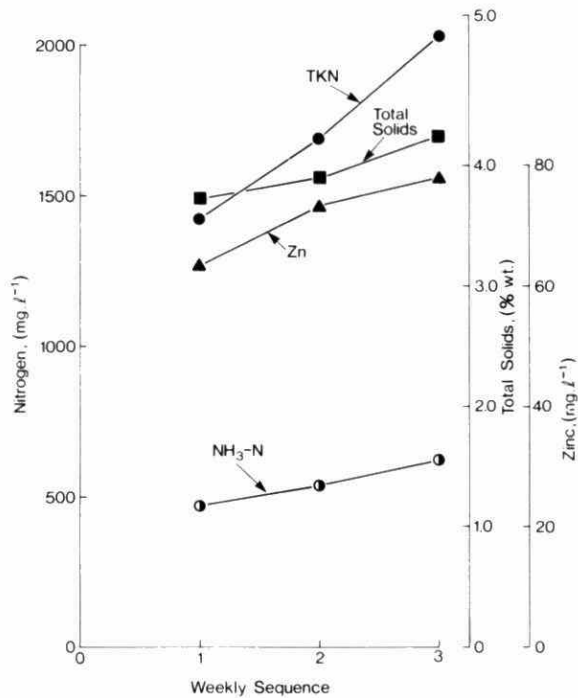DAYS WITHIN WEEKS, CHATHAM WPCP

FIGURE 4. MEAN PARAMETER CONCENTRATIONS BETWEEN
SAMPLES WITHIN DAYS, CHATHAM WPCP

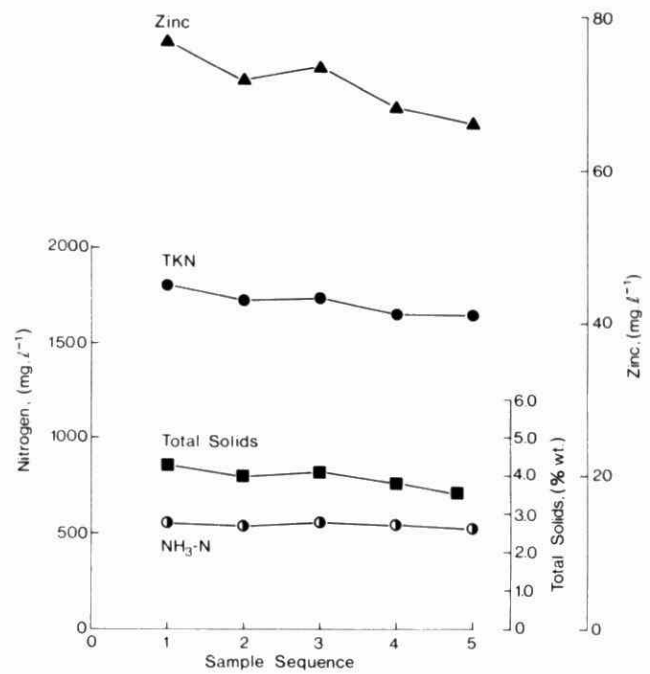FIGURE 5. MEAN PARAMETER CONCENTRATIONS BETWEEN
WEEKS, CHATHAM WPCP

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TABLE 8. ANALYSIS OF VARIANCE, CHATHAM SLUDGE

Source of Variation	df	Total Solids			TKN		
		Mean Square	Significance	$s^2(\%)^2$	Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$
Between weekly periods	2	4.823441	*	0.0427594	7,011,136	**	82,296
Between days within weeks	12	1.616485	NS	0.0504925	838,933	**	50,253
Between samples within days	60	0.859098	**	0.2847794	85,144	**	23,560
Between repeats within samples	150	0.00475953		0.0047595	14,464		14,464

Source of Variation	df	NH₃-N			Zinc		
		Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$	Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$
Between weekly periods	2	428,795	**	5,685	4,265	**	49.7
Between days within weeks	12	2,566	*	97	535	*	19.2
Between samples within days	60	1,118	**	313	247	**	74.1
Between repeats within samples	150	179		179	24.6		24.6

* Significant at 95% level.
** Significant at 99% level.
NS Not significant at 95% level.

TABLE 9. ANALYSIS OF VARIANCE, MILTON SLUDGE

Source of Variation	df	Total Solids			TKN		
		Mean Square	Significance	$s^2(\%)^2$	Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$
Between daily periods	24	2.4390	NS	0.0	300,580	NS	0
Between batch loads within days	37	2.3992	**	0.5376	433,236	**	75,426
Between samples within batches	124	0.2660	**	0.1922	140,520	**	95,645
Between repeats within samples	68	0.0104		0.0104	13,312		13,312

Source of Variation	df	NH_3-N			Zinc		
		Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$	Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$
Between daily periods	24	28,551.50	**	2,108.68	256.9241	NS	0.4985
Between batch loads within days	37	6,649.95	**	895.56	231.3479	**	49.7445
Between samples within batches	124	3,036.68	**	1,516.28	33.8519	**	20.1070
Between repeats within samples	68	1,020.03		1,020.03	7.1096		7.1096

** Significant at 99% level.
NS Not significant at 95% level.

Mean parameter concentrations between batches within days, between days, and between samples within batches are depicted in Figures 6, 7, and 8, respectively. TKN, total solids, and zinc declined in concentration within a batch, while ammonia remained relatively constant from sample to sample (Figure 8). Between batch loads within a day, TKN, total solids, and zinc were highly variable (Figure 6). Ammonia displayed slight variability from batch-to-batch. Parameter concentrations from day-to-day at Milton are depicted in Figure 7. Between days, ammonia exhibited less variability than TKN, total solids, and zinc.

Highly significant differences were detected between samples within batches and between batch loads within days for all four parameters. Only ammonia exhibited a significant difference between days; the others were not significant (Table 9). A trend test (Kendall, 1970) revealed that the ammonia concentration in the digested sludge had decreased significantly during the study period.

Separation of the components of variance indicated that most variability was a result of differences between samples within a batch and of differences between batches within a day. Contributions to overall variance from sampling, analytical, and testing error were small. For ammonia, however, differences between days contributed the most to variability; this was due partly to a longer term trend in the NH_3-N concentrations.

Owing to large contributions to the overall variability from "within batch" and "between batches" heterogeneity, estimates of the component of variance for "between days" variability were sometimes negligible. Through estimation errors, these variances were frequently negative in sign, but were interpreted as zero values for practical purposes (Table 9). This observation emphasizes the need for efficient sampling within a day at any plant with similar characteristics. Variability between days is apparently obscured by this within day heterogeneity.
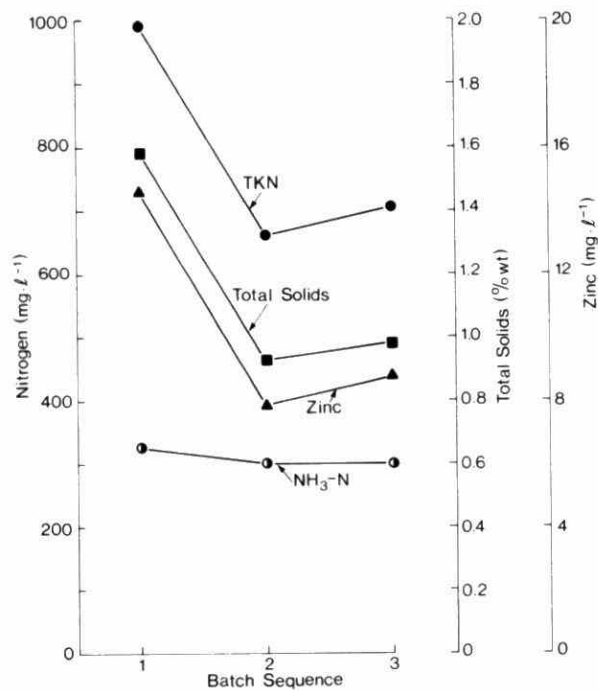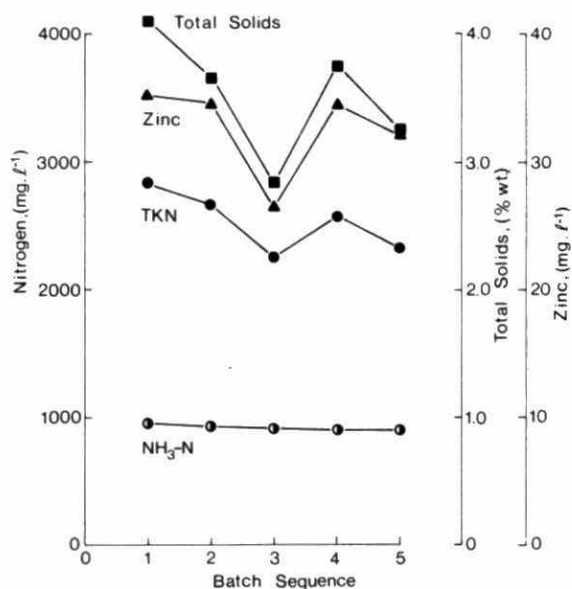
FIGURE 6 MEAN PARAMETER CONCENTRATIONS BETWEEN BATCHES WITHIN DAYS, MILTON WPCP
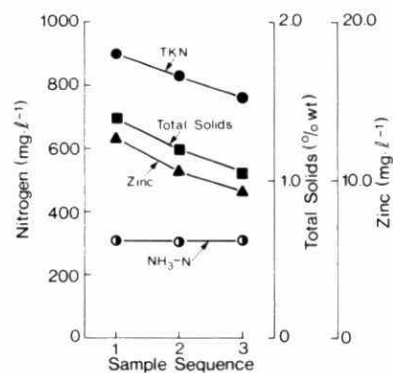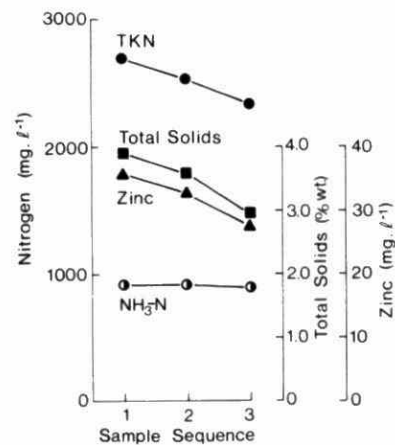

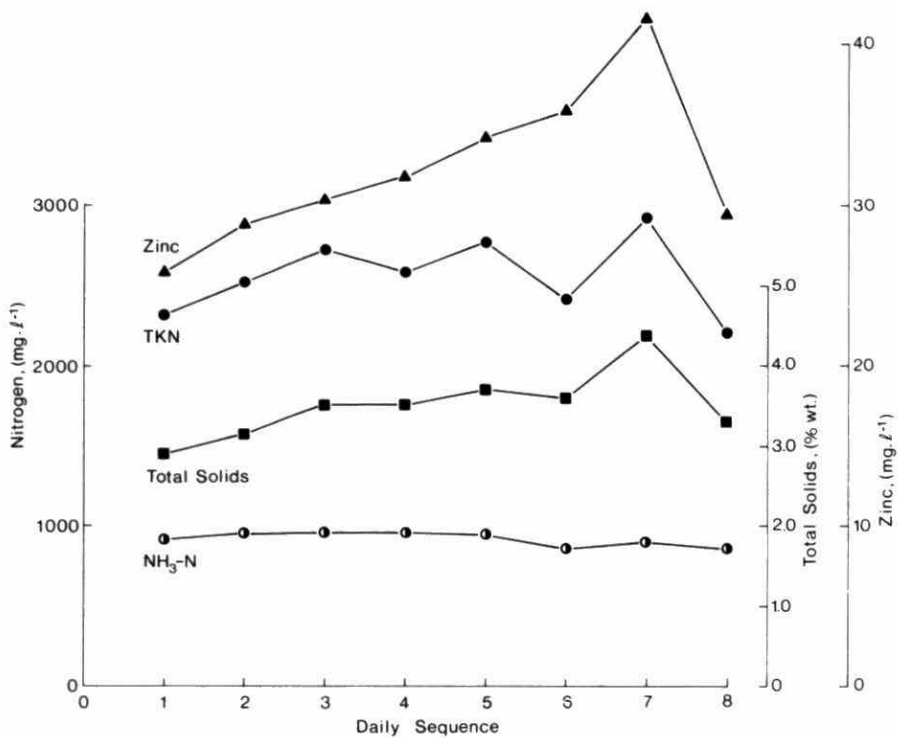FIGURE 8 MEAN PARAMETER CONCENTRATIONS BETWEEN SAMPLES WITHIN BATCHES, MILTON WPCP
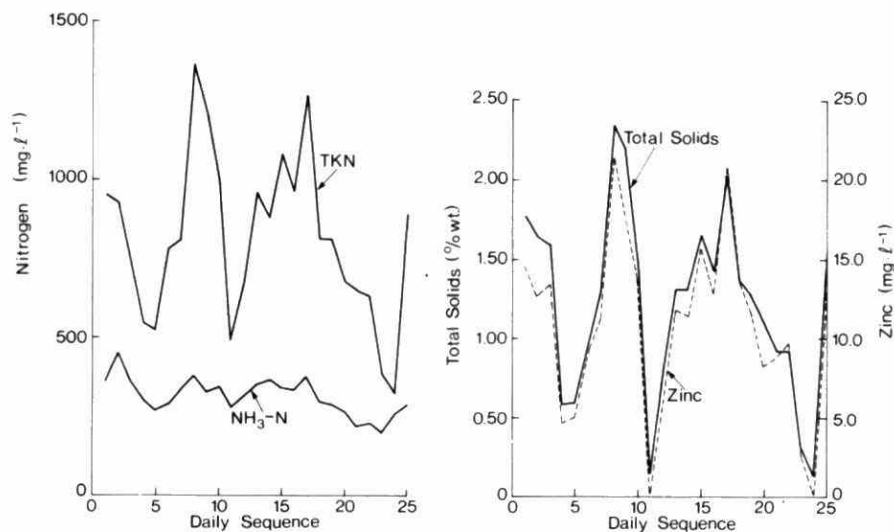
FIGURE 7 MEAN PARAMETER CONCENTRATIONS BETWEEN DAYS, MILTON WPCP

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The data suggest that the particular process of sludge treatment and disposal at this plant may require some modification in order to decrease within day variability. The large variability observed within a day is reflected in the number of batches needed in the optimum allocation of resources (Table 6). It is apparent from the ANOVA (Table 9) and Table 6 that more effort will be required to characterize this sludge with the same degree of precision as any of the other plants assessed in this study.

4.4   Oakville S.E. WPCP

Relevant statistical data for the parameters under study in digested sludge from the Oakville S.E. WPCP are summarized in Table 4. An unbalanced ANOVA, similar in design to that used at Milton, was generated; the results are presented in Table 10.

Mean parameter concentrations between batches within days, between days, and between samples within batches are shown in Figures 9, 10, and 11, respectively. Mean sample concentrations within a batch for TKN, total solids, and zinc decreased continually. Ammonia remained relatively constant within a batch (Figure 11); this behaviour was also observed at the Milton WPCP. Considerably more variation from batch-to-batch existed for TKN, total solids, and zinc than existed for ammonia; average total solids dropped from over 4% to less than 3% in the first three batches. The increase in the fourth batch (Figure 9) was attributed to transfer of the pump suction point to a different sump in the digester. This was usually done by the operator when he visually observed a decrease in the feed solids. Increasing concentrations of TKN, total solids, and zinc occurred until the final sampling day (Figure 10). Ammonia did not display this increase.

Highly significant differences were detected between samples within batch loads and between batches within days for all parameters. No significant difference was detected between days (Table 10).

In this sludge, the component of variance contributing most to overall variability arose between samples within a batch, followed by the between batches within a day component. The contribution to variability from sampling, analysis and testing was small, and the least

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TABLE 10. ANALYSIS OF VARIANCE, OAKVILLE S.E. SLUDGE

Source of Variation	df	Total Solids			TKN		
		Mean Square	Significance	$s^2(\%)^2$	Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$
Between daily periods	7	4.64004	NS	0.0	1,256,260	NS	7,770
Between batches within days	25	6.73660	**	0.9841	1,046,540	**	149,820
Between samples within batches	66	2.26996	**	1.4225	369,760	**	186,940
Between repeats within samples	48	0.22156		0.2216	100,570		100,570

Source of Variation	df	NH₃-N			Zinc		
		Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$	Mean Square	Significance	$s^2(mg \cdot l^{-1})^2$
Between daily periods	7	15,745.7	NS	0.0	558.48	NS	0.0
Between batches within days	25	19,828.9	**	3,558.1	570.35	**	77.44
Between samples within batches	66	3,996.5	**	2,252.6	217.53	**	123.68
Between repeats within samples	48	752.8		752.8	39.43		39.43

** Significant at 99% level.
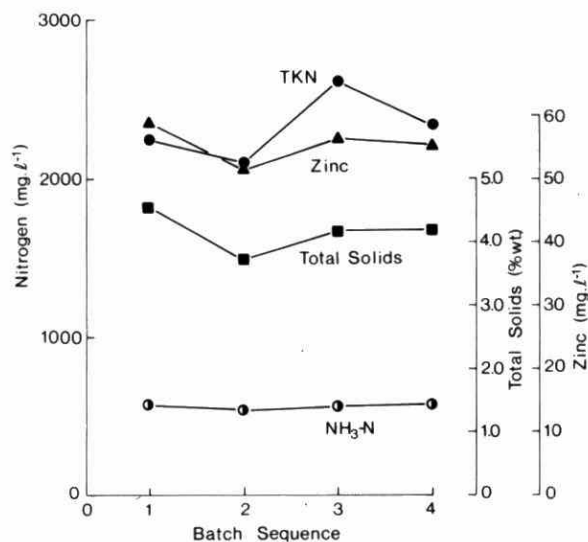NS Not significant at 95% level.

FIGURE 9. MEAN PARAMETER CONCENTRATIONS
BETWEEN BATCHES WITHIN DAYS,
OAKVILLE S.E. WPCP

FIGURE 11. MEAN PARAMETER CONCENTRATIONS
BETWEEN SAMPLES WITHIN BATCHES,
OAKVILLE S.E. WPCP

FIGURE 10. MEAN PARAMETER CONCENTRATIONS BETWEEN DAYS, OAKVILLE S.E. WPCP

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contribution to variance was evident in the source of variation attributed to differences between days. Here, negative components of variance frequently were calculated, indicating that differences between days were negligible in comparison with the other components. Zeros were substituted for these negative values (Table 10). The optimum sampling allocation for Oakville S.E. is given in Table 6. To characterize product sludge with a precision equivalent to precisions at WPCP's dewatering sludge, the data collected at the Oakville site suggest that plants disposing sludge batchwise will have to expend additional effort. In practical terms, more samples will be required. The data also suggest that real differences occur between a sequence of batches discharged within the same day; with the exception of NH_3-N, these differences are great enough to cause concern.

4.5   Tillsonburg WPCP

A statistical summary of the parameters in Tillsonburg sludge is presented in Table 4; the ANOVA is summarized in Table 11. Only differences between batch loads and within batch loads could be assessed because of a limited sampling program. Samples were collected from the tank truck outlet at the disposal site; this was the major difference when comparing this program with the sampling programs at the Milton and Oakville S.E. WPCP's. A statistical summary of the parameters in Tillsonburg sludge is presented in Table 4; the ANOVA is summarized in Table 11.

More variability was observed between batch means for TKN, total solids, and zinc than for ammonia (Figure 12). At this WPCP, each batch assessed was discharged from the digester on a different day. Sample means within batches were approximately constant for ammonia, total solids, and zinc; TKN exhibited more variability within a batch, but this variability remains unexplained (Figure 13).

Significant differences were detected between batch means (sampled on different days) for ammonia, TKN, total solids, and zinc (Table 11). Separation of the components of variance revealed that the difference between batch means was the chief source of variability for total solids and zinc; for TKN the differences within batches contributed

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TABLE 11. ANALYSIS OF VARIANCE, TILLSONBURG SLUDGE

Source of Variation	df	Total Solids			TKN		
		Mean Square	Significance	$s^2(mg \cdot 1^{-1})^2$	Mean Square	Significance	$s^2(mg \cdot 1^{-1})^2$
Between batches	3	1.169×10^8	**	1.17×10^7	453,450	*	31,380
Within batches	36	1.778×10^5		1.78×10^5	139,646		139,646

Source of Variation	df	NH_3-N			Zinc		
		Mean Square	Significance	$s^2(mg \cdot 1^{-1})^2$	Mean Square	Significance	$s^2(mg \cdot 1^{-1})^2$
Between batches	3	1,284	**	114	91.5	**	9.1
Within batches	36	145		145	0.38		0.38

* Significant at 95% level.
** Significant at 99% level.

FIGURE 12. MEAN PARAMETER CONCENTRATIONS
BETWEEN BATCHES, TILLSONBURG WPCP
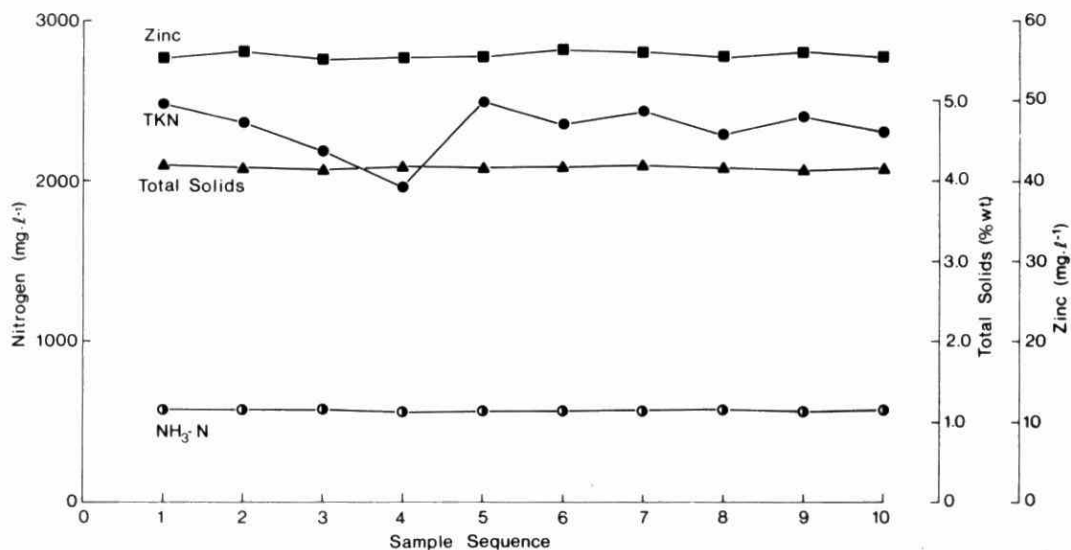
FIGURE 13. MEAN PARAMETER CONCENTRATIONS BETWEEN SAMPLES WITHIN BATCHES, TILLSONBURG WPCP

most to the variability. The components of variance for ammonia were nearly equal, the variability within batches being slightly larger; the real variations (Figures 12 and 13) were almost undetectable. Optimum allocation of sampling resources for Tillsonburg sludge is summarized in Table 6.

The Tillsonburg WPCP data suggest that the process of mixing during filling a tank truck, and the transit to a disposal site, is effective in reducing the variations in the feed to discrete batches which were observed at the Milton and Oakville S.E. WPCP's. Data to demonstrate variations in batch feeds, or variations between batches within days at this plant were not collected. It is expected, however, that significant differences do occur from these sources on the basis of data from the other plants. One can conclude that a relatively homogeneous mixture is spread onto farm land from one batch, but significant differences for solid phase contaminants may be expected from batch-to-batch within the same day.

4.6   Analysis of Long Term Records

4.6.1   Extended sampling program, Chatham WPCP

A sampling program was conducted at the Chatham WPCP (June to November 1975) to determine the variability of digested sludge during a period of about five months. This study also served as a diagnostic check for the short term sampling survey carried out in March, 1975. The concentration fluctuations are shown in Figure 14. Comparison of this long record with the results from the intensive sampling program in March brings to light the following:

1.   In June, concentrations of Zn and Ni were the same as in March, while NH_3-N and Cu concentrations had increased. TKN and total solids were variable, but had the same magnitude as in March (Table 4 and Appendix II).

2. NH_3-N concentration showed a gradual decrease during the course of the program. Ni remained constant through the June to November study.
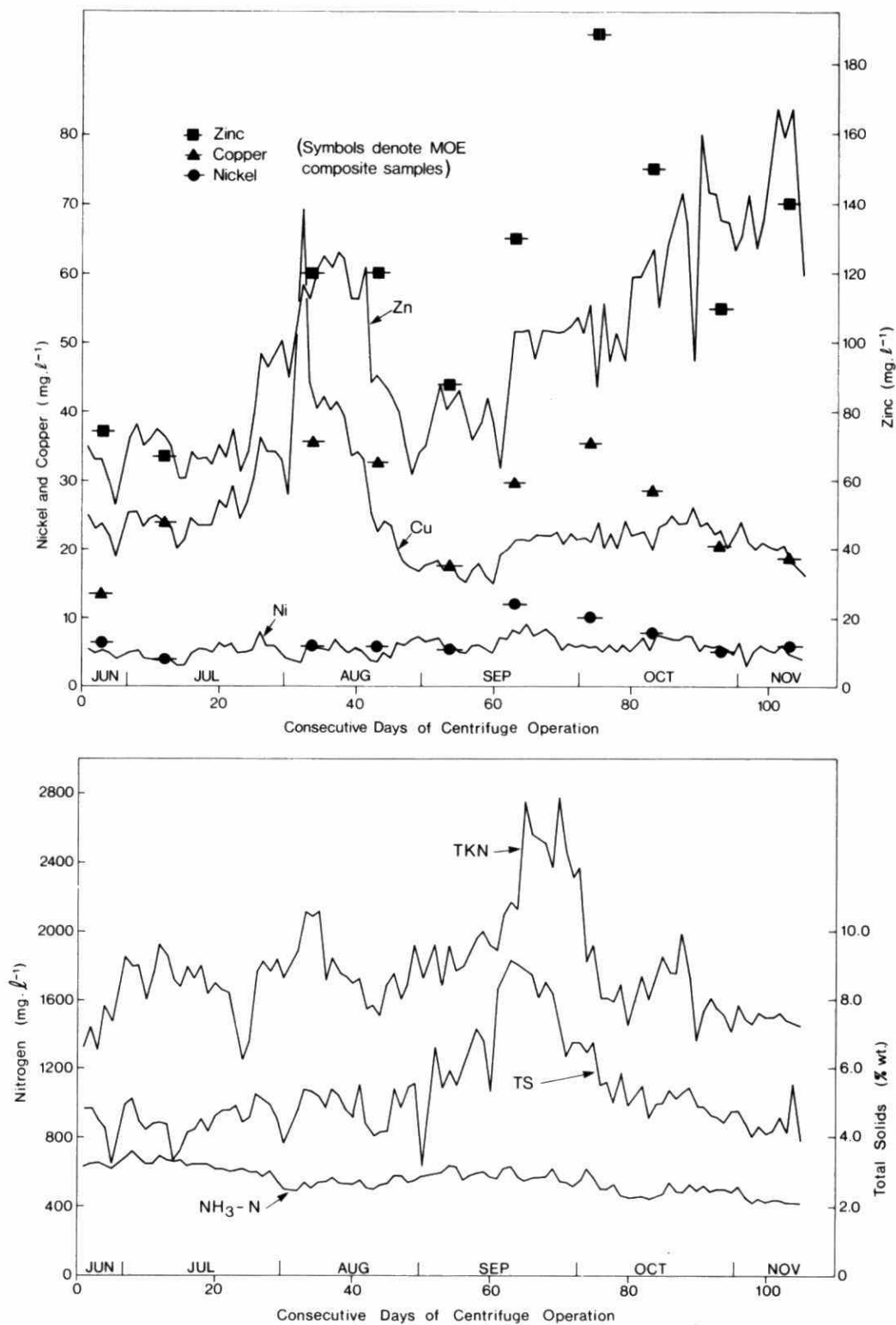
FIGURE 14. VARIATION OF PARAMETER CONCENTRATIONS, CHATHAM WPCP, JUNE 23 TO NOVEMBER 14, 1975

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3. In July and August, Zn and Cu concentrations increased temporarily, indicating a possible contribution from an industrial source. These metals returned to mean "background" levels in mid-September.

4. Zn increased from mid-September onwards; by late October, the concentration was approximately twice as high as in June. It would appear that the sewage was receiving Zn from a new source.

5. Total solids showed a maximum in September and this was attributed to the peak fruit and vegetable processing season which started in August.

As a diagnostic check, the lengthier survey emphasized the variability exhibited by digested sludge. Although the concentrations in June were similar to those measured in March, fluctuations were detected with time. It is also clear from Figure 14 that total solids and heavy metals are not necessarily correlated, even at the same WPCP. The use of such correlations for prediction purposes could be misleading.

A survey of heavy metal concentrations in digested sludge at the Chatham WPCP was carried out concurrently by the Ontario Ministry of the Environment (MOE). A digested sludge composite sample was analyzed for heavy metals every other week. MOE data for nickel, copper, and zinc from late June to the middle of November are given in Figure 14. Most of the sample points compare favourably with the data which were collected in the supplementary survey. With one exception for zinc during October, the independent samples and the supplementary survey samples did not differ more than might have been expected (cf. Section 5.1). The larger deviations do emphasize the need for well designed and consistent sampling strategies. To some extent, the deviations can be accounted for by the factors identified in the short term sampling surveys.

4.6.2   Analysis of long term solids records, Chatham WPCP

The staff of the Chatham WPCP maintained a record of the total and volatile solids content of raw and digested sludges. Raw, primary

clarified solids concentration records consisted of the results of a
single grab sample collected once per week. Secondary digested sludge
solids concentrations were determined in single grab samples taken once
per weekday; the data were condensed, however, to an arithmetic average
weekly value. Records from January, 1973 to November, 1975 were avail-
able for raw, primary clarified sludge (Figure 15), and from July, 1973
to November, 1975 for digested sludge (Figure 16). Although the past
plant sampling procedure was not as rigorous as the more efficient
sampling arrangement identified in this project, the long sequence of
observations provided an excellent opportunity to identify any serial
dependency in the data.

Digested sludge solids concentrations from May, 1974 to
May, 1975 were examined using mean weekly concentrations (mean of five
days' results) to determine the inherent variation. The grand mean was
4.6% solids by weight with an RSD of 22%. For an RSD of 22%, the sample
size plot (Section 1-3, Appendix 1) indicated that 19 samples were
needed during the year to estimate the mean within ±10% of its true
value. A daily composite sludge sample should be collected at the plant
every two to three weeks to satisfy this requirement.

The RSD for total solids in Chatham digested sludge during one
year has the same magnitude as the RSD values estimated for other pro-
cess streams in a survey of eight treatment plants from across North
America (Thomann, 1970). Over one year, the RSD's for BOD in sewage
influent ranged from 17 to 33%, while the RSD's for primary effluent BOD
varied from 21 to 39% in that study. The RSD's of plant flow for one
year ranged from 14 to 32% (Thomann, 1970). Chatham digested sludge
solids reflect the variation inherent in the input to the sewage treat-
ment process.

Probability distributions for total solids in raw sludge
showed that the values were approximately normally distributed (Figure
17). The median value for the series was 3.9% with a range of 2.3 to
8.6%. The digested sludge solids did not depart greatly from a normal
distribution (Figure 17). The median value was 4.2% with a range of
2.9 to 8.8%.
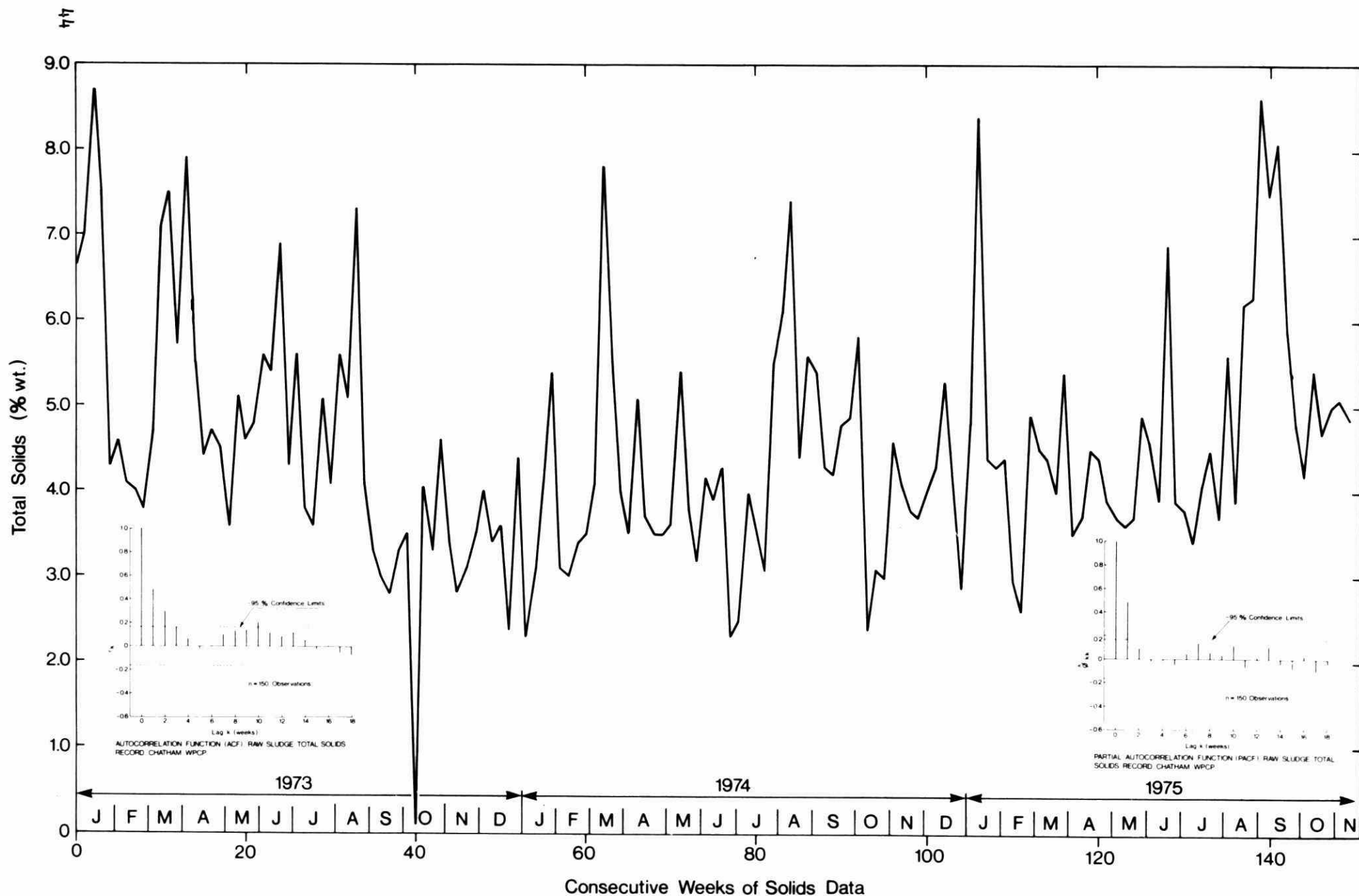
FIGURE 15. WEEKLY RAW SLUDGE SOLIDS CONCENTRATIONS, CHATHAM WPCP, 1973-1975
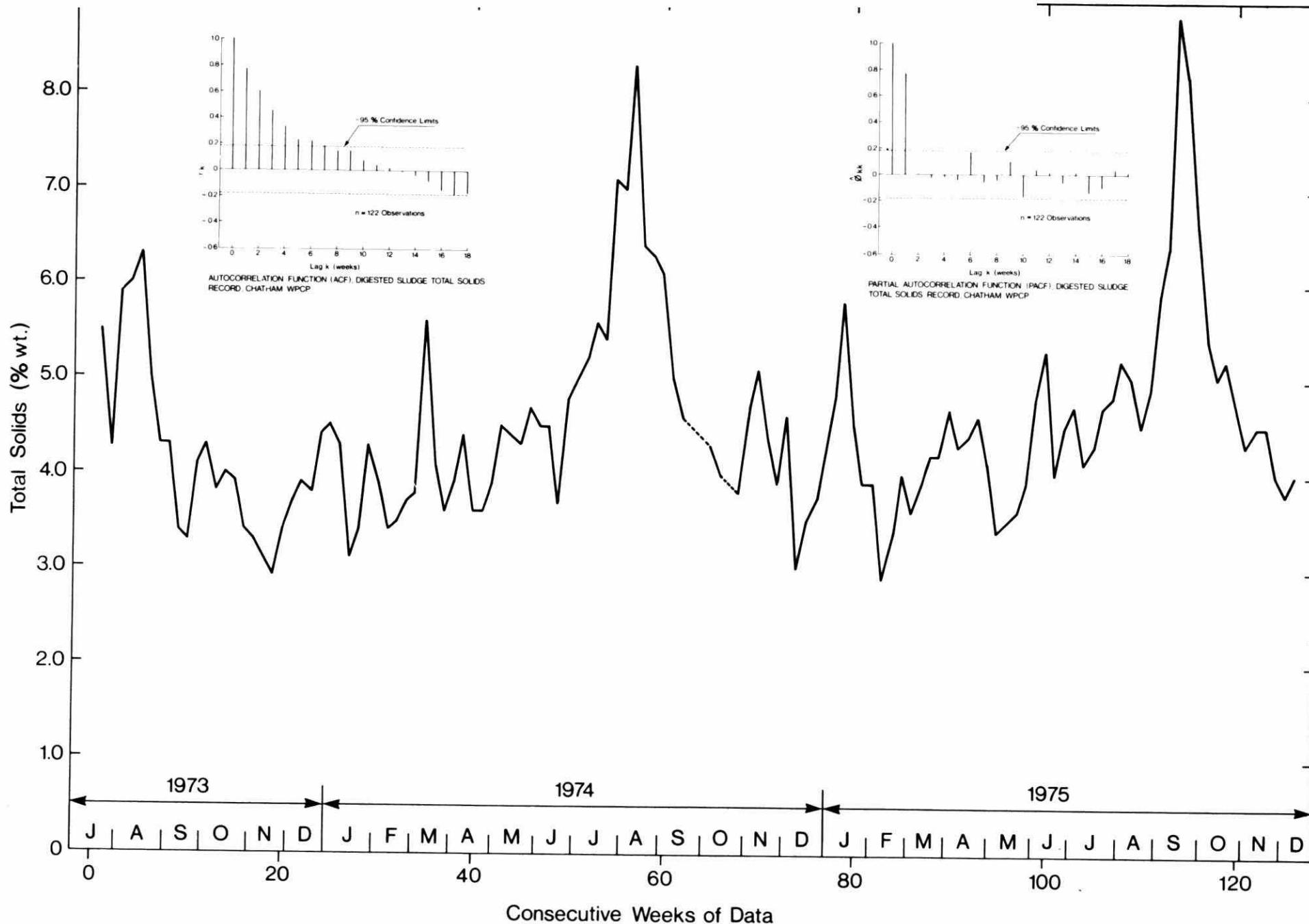
FIGURE 16. WEEKLY DIGESTED SLUDGE SOLIDS CONCENTRATIONS, CHATHAM WPCP, 1973-1975 (Dashed Lines Indicate Missing Data)
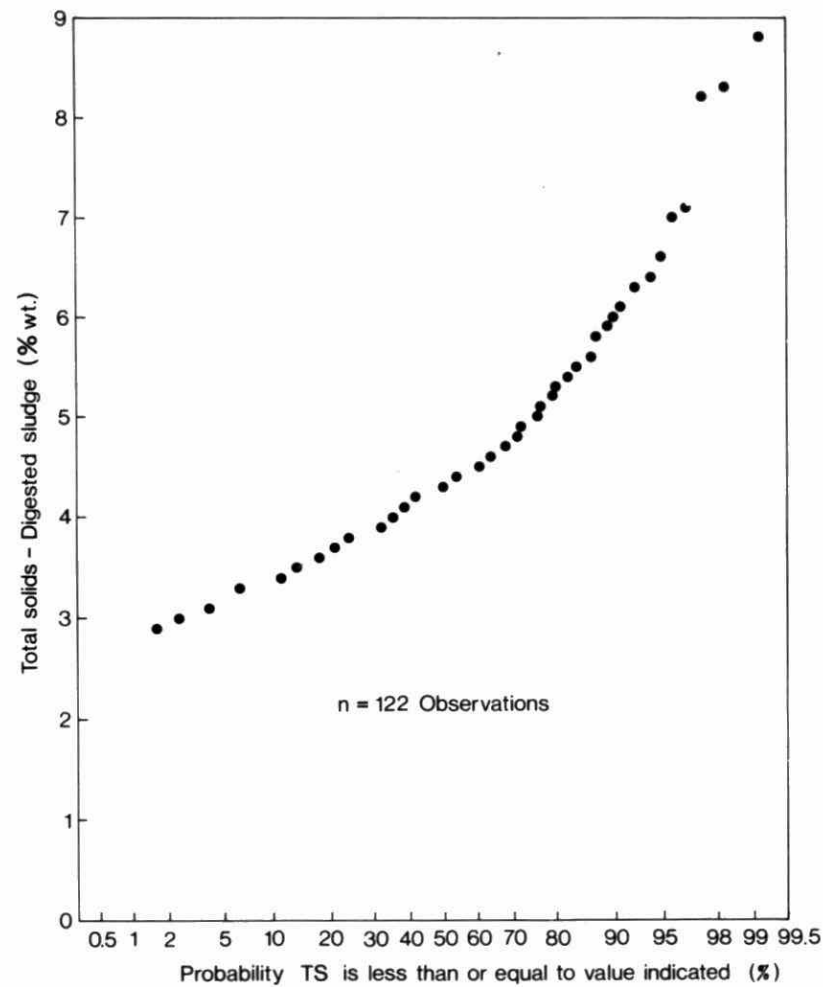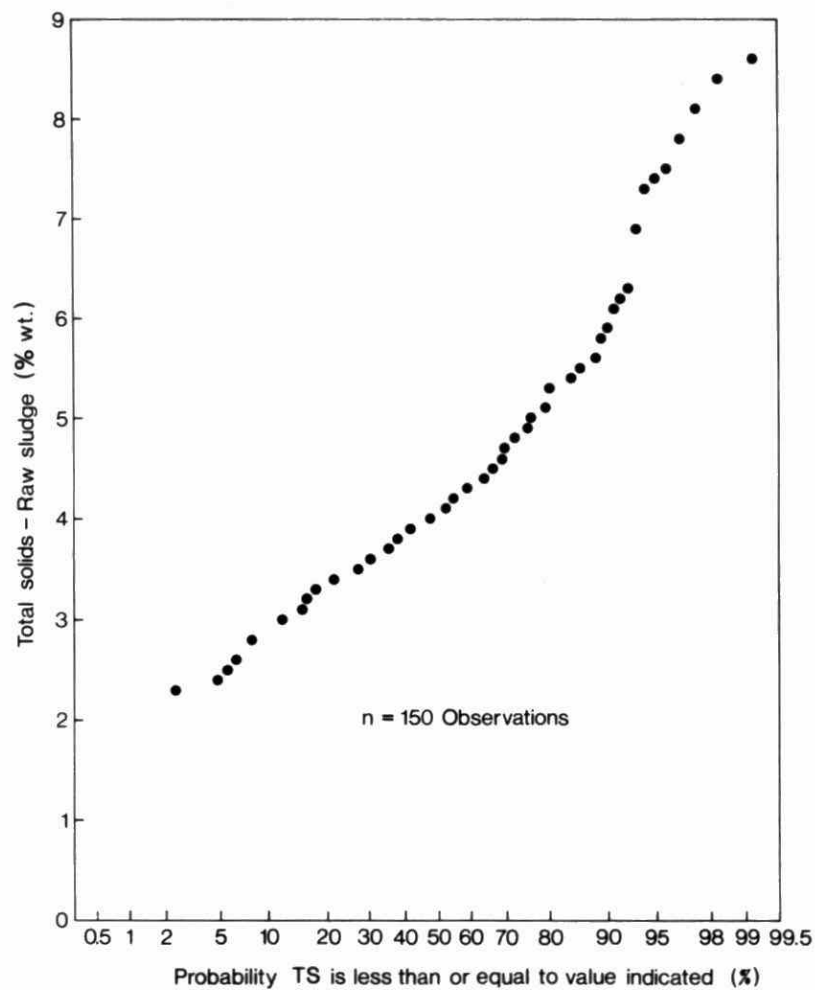
FIGURE 17. PROBABILITY DISTRIBUTIONS OF RAW AND DIGESTED SLUDGE SOLIDS CONCENTRATIONS, CHATHAM WPCP, 1973-1975

The autocorrelation function (ACF) and partial autocorrelation function (PACF) for the raw sludge total solids sequence indicated that the time series was stationary (Figure 15). Stationarity implies that the series is characterized by a mean which is constant with time. These functions also suggest that the process response was not random, and observations one or two weeks apart were dependent. The ACF indicated a significant correlation at lag 10; a 'spike' in the record occurs about every 10 weeks. Since the significant correlation at lag 10 of the ACF is weak and the PACF for lags >1 is random in nature, an autoregressive model can be tentatively entertained as a simple characterization of the raw sludge data. The fixed solids data were characterized in the same manner since they too showed a similar ACF and PACF, but without significance at lag 10. An autoregressive interpretation implies that a "present value" of concentration is correlated to previous values of itself, and is a function of these values plus a random deviation associated with the process. For the total solids concentration, the relatively low magnitude of the ACF at lag 1 implies that the relationship to previous values may not be particularly strong, and that randomness plays an important role in characterizing the data. This can be partly accounted for by the lack of available data, since only single weekly grab samples were analyzed. Nevertheless, the analysis gives insight into the nature of the raw sludge solids characteristics.

The digested sludge total solids data can also be characterized by a first order, stationary, autoregressive process. The ACF shows exponential decay, and the PACF tentatively confirms the autoregressive process, since it lacks significance for lags >1 (Figure 16). The relationship of the total solids in the digested sludge to previous values is more significant than in the case of raw sludge solids. This is clearly shown by the large correlation coefficient associated with the first lag of the ACF in Figure 16. Considering the better quality of the data, the higher degree of correlation is understandable. The digestion system is expected to dampen variations in its feed, and to provide a more homogenized product with similar composition from one period to the next. A period in this case was one week.

The nature of a process with an ACF almost identical to the ACF for the digested sludge total solids sequence (Figure 16) has been discussed elsewhere (Box and Jenkins, 1970, pp. 57-58). Box and Jenkins indicate that such a series is characterized by similarity in neighbouring values and exhibition of marked trends. Clearly, inspection of the time series reinforces these remarks (Figure 16). Trends are observed in the formation of peaks and troughs in the data. This is especially noticed in the large peaks which are attributed to the seasonal fruit and vegetable processing industry in this community. The industry is generally in full production in the summer months. Unfortunately, a lack of data prevents identification of this effect as a seasonal component in the time series analysis.

The underlying time series process identification indicates that the series is not random on a long term basis, and once a deviate observation is obtained more deviations may be expected. In this case a constant mean aids in characterizing the system in the long term; the process does not drift from the mean for excessively long periods of time. The autoregressive process implies that more frequent sampling after a major deviation would help to characterize the product. This procedure has been discussed in a similar application for monitoring stream quality (Arnold, 1970). This suggests that more attention be paid by plant operating personnel to the product sludge at plants where similar stochastic processes are identified. The use of control charts (cf. Section 5.3) to monitor solids content might be useful in this regard, with more frequent sampling when the process is "out of control".

A substantial random component can be expected in the digestion process even when a dependent series has been identified as at Chatham. This has been discussed with regard to the nature of performance variability of water pollution control plants which are regionally related (Adams and Gemmell, 1973). These authors suggest that non-random behaviour is frequently observed on a long term basis, but a random behaviour predominates in the short term. They believe, however, that a random component is also important in the long term. For the digested sludge solids data presented here, the serial dependency is much stronger than the dependency for the observations of Adams and Gemmell.

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The relationship between secondary digested sludge total solids and raw, primary clarified sludge solids is best identified by the cross correlation function (CCF) for these two tentatively stationary time series (Figure 18). Inspection of the two series (Figures 15 and 16) shows that peak values have some correspondence. The CCF demonstrated significant cross correlations up to lag 3 with the impulse response function decreasing exponentially from the starting point at lag zero. The significant impulse at lag zero implies that the delay time in observation of an effect in the output (digested sludge) due to a perturbation in the input (raw sludge) was less than the sampling interval. This is the expected characteristic for completely stirred tank reactors in series. An important implication of this observation is that impulses in the input, efficiently damped by complete mixing in the primary digestion system, will be further damped in the secondary digester. But the RTD study at the Chatham WPCP demonstrated that the primary digester was not completely utilized (Section 4.8.3). Departures from the ideal complete mix state have been briefly discussed by Knopp (1967), and Novotny and Stein (1976), who indicate that the gain of a system is increased when disrupted by stagnant regions or bypass flow.

The long term data were also used in conjunction with the ACF to obtain an estimate of the optimum sampling frequency (Bendat and Piersol, 1966; Wallace and Zollman, 1971). For digested sludge total solids, the ACF indicated that observations approximately four weeks apart were uncorrelated. Using the safety factor of two suggested by Wallace and Zollman, the sampling frequency should be about two weeks. Inspection of the data (Figure 16) indicated that a two-week sampling frequency should adequately reveal the variance associated with the system, yet should not overburden the operating personnel. However, knowledge of "within day" variability must be used to ensure representative sampling. Operating experience should supply this knowledge. At Chatham, it is suggested that three or four samples judiciously selected on one day every two weeks would be representative. These samples may be composited for analysis. In addition, it is suggested that varying the day within the sampling week should overcome any hidden bias when sampling always on the same day.
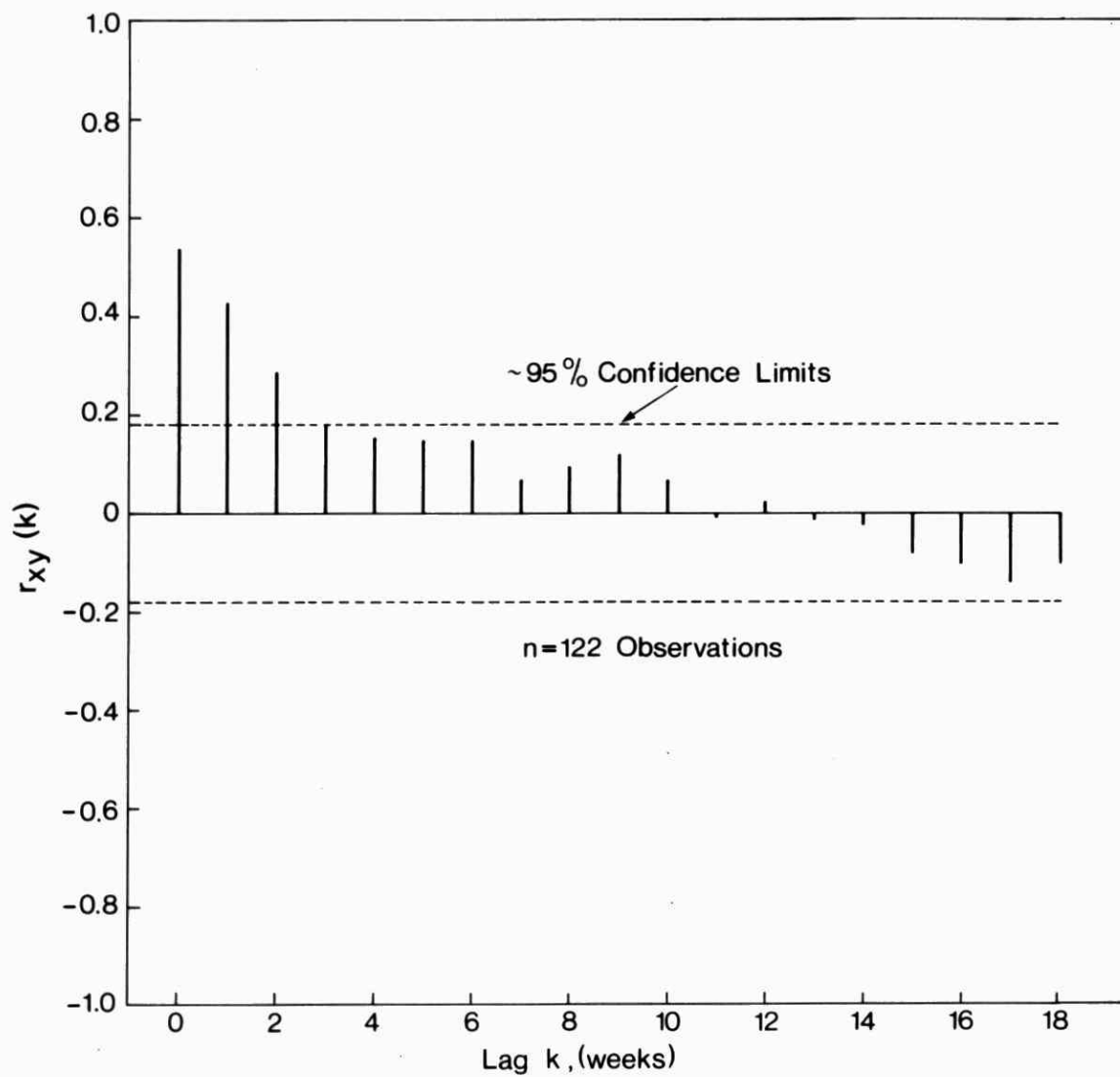
FIGURE 18. CROSS CORRELATION FUNCTION BETWEEN RAW AND DIGESTED
SLUDGE TOTAL SOLIDS AT ONE WEEK INTERVALS,
CHATHAM WPCP, 1973-1975

4.6.3   Analysis of long term solids records, Tillsonburg WPCP

Total solids records were examined for the Tillsonburg WPCP
for an interval extending from January, 1974 to November, 1975. Single
grab samples were collected weekly from both the raw sludge and digested
sludge transfer lines by plant personnel. Although it may be argued
that this manner of sampling is unrepresentative, these are the only
long term data available. Digested sludge samples were collected at the
time of filling a tank truck which was used to haul the sludge to land
disposal sites.

The grand mean of weekly digested sludge solids observations
for about one year (January 2 to December 17, 1974) was 4.2% solids by
weight. The resulting RSD for this period was 16%, which was less than
the RSD observed for one year of solids results from Chatham. There
was, however, no peak food processing season which did contribute to the
overall solids variability at Chatham. For a RSD of 16%, the sample
size plot (Section 1-2, Appendix 1) revealed that 10 samples were
necessary during one year to achieve a precision of ±10% in the mean
solid concentration.

Few patterns can be observed in the total solids record for
the raw sludge data (Figure 19). A probability plot of this data
indicated that the underlying distribution was approximately normal
(Figure 20); the values ranged from about 2 to 5.5%. The ACF (Figure
19) revealed that the time series was a stationary, random process. The
observations at one-week intervals were apparently uncorrelated, and
characterized by a constant mean of 3.37% with standard deviation 0.65%.
These characteristics show that this particular plant was not influenced
by any substantial trends or seasonal processes as observed for the
Chatham WPCP (Section 4.6.2).

The digested sludge total solids series also lacked the
appearance of any marked trends (Figure 21). A probability plot of this
data showed an approximately normally distributed series with a few low
values (Figure 20). The series had a mean of 4.1% solids with standard
deviation 0.45%. The low values occur early in the series depicted in
Figure 21. The ACF of the original series indicated significance at the

51
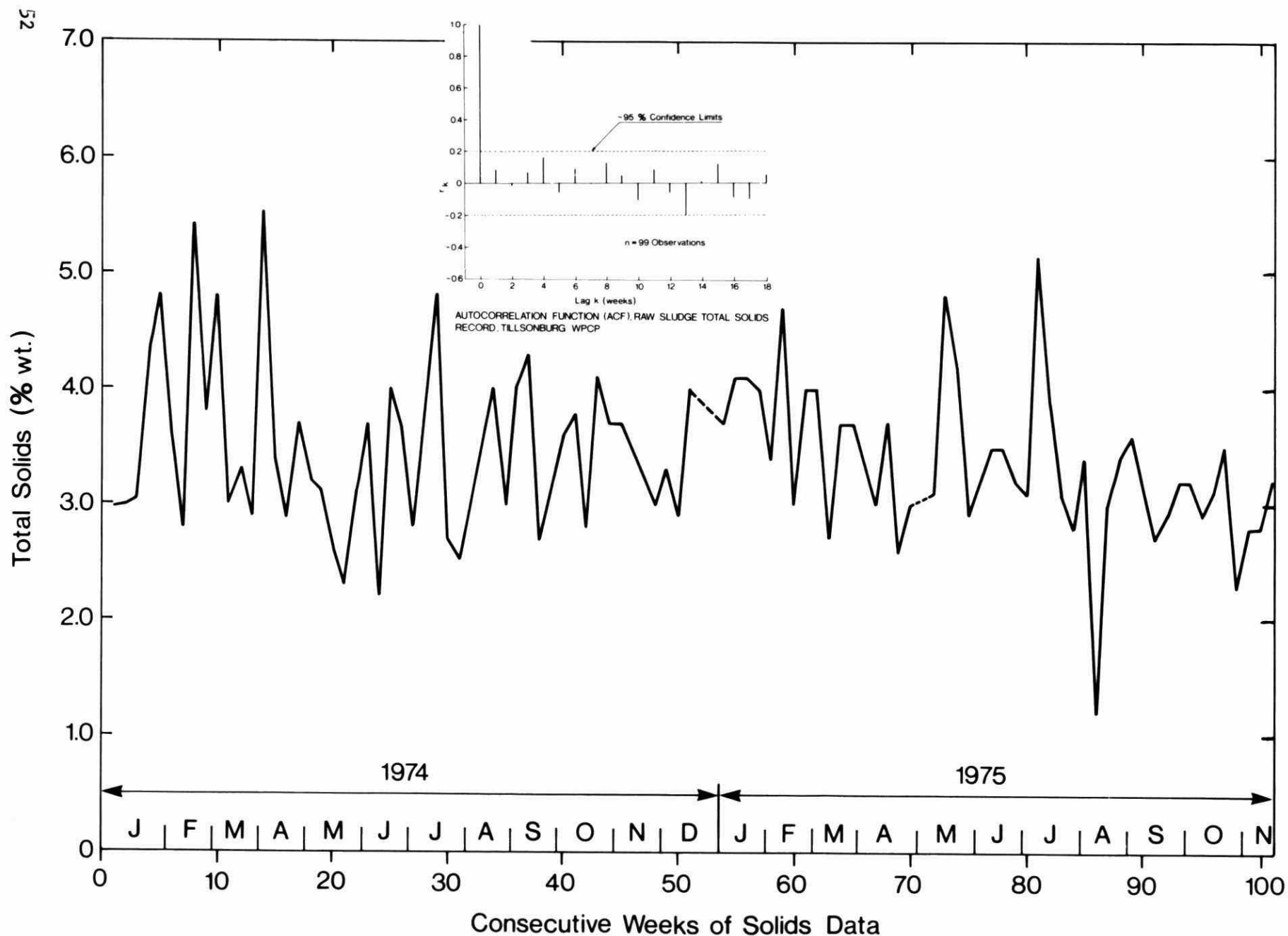
FIGURE 19. WEEKLY RAW SLUDGE SOLIDS CONCENTRATIONS, TILLSONBURG WPCP
1974-1975 (Dashed Lines Indicate Missing Data)
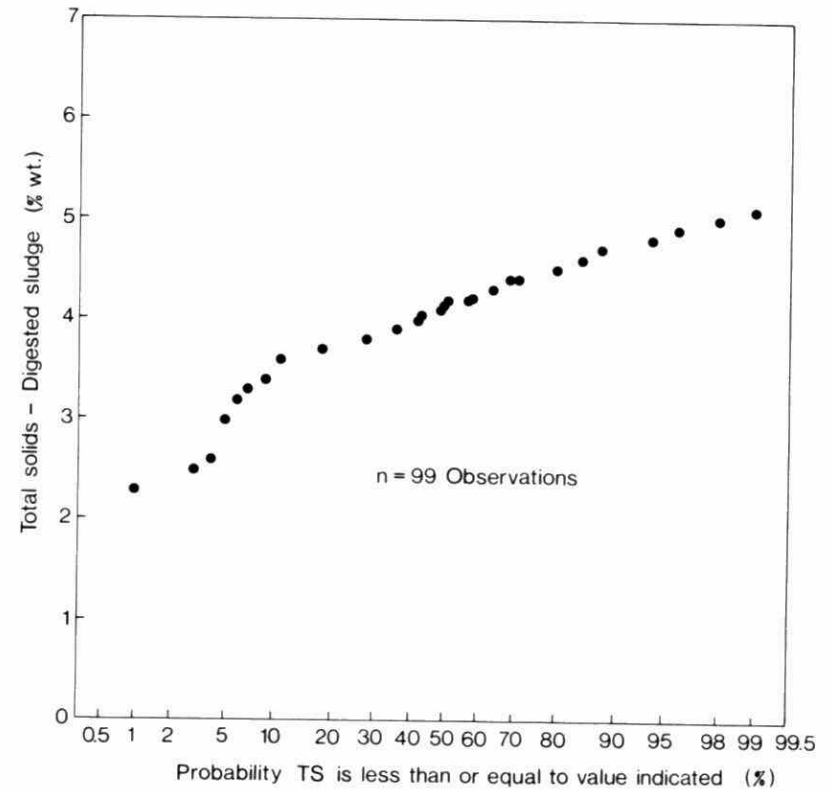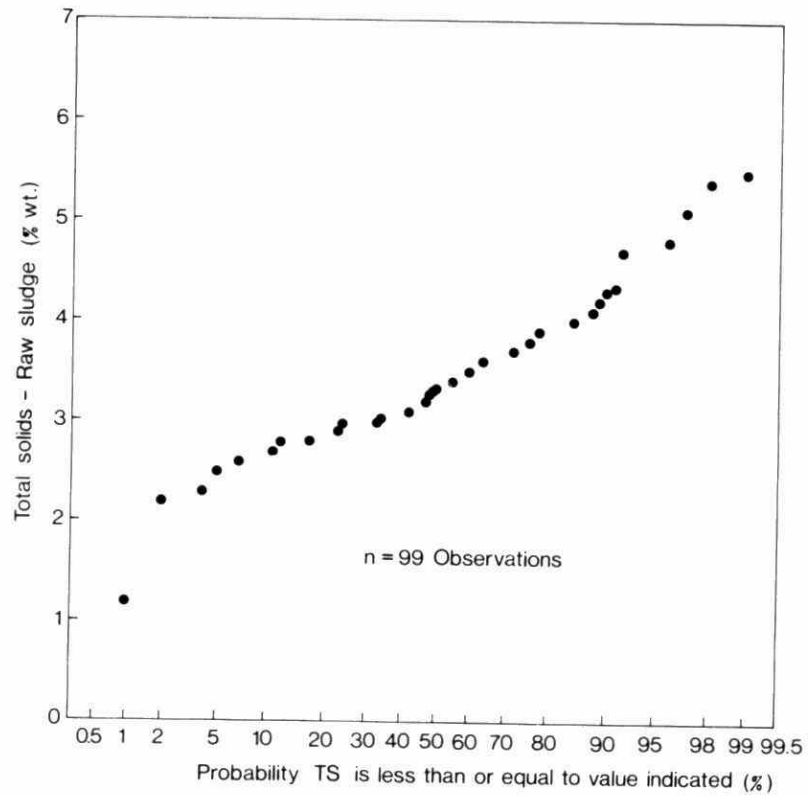
FIGURE 20. PROBABILITY DISTRIBUTIONS OF WEEKLY RAW AND DIGESTED SLUDGE SOLIDS CONCENTRATIONS, TILLSONBURG WPCP, 1974–1975
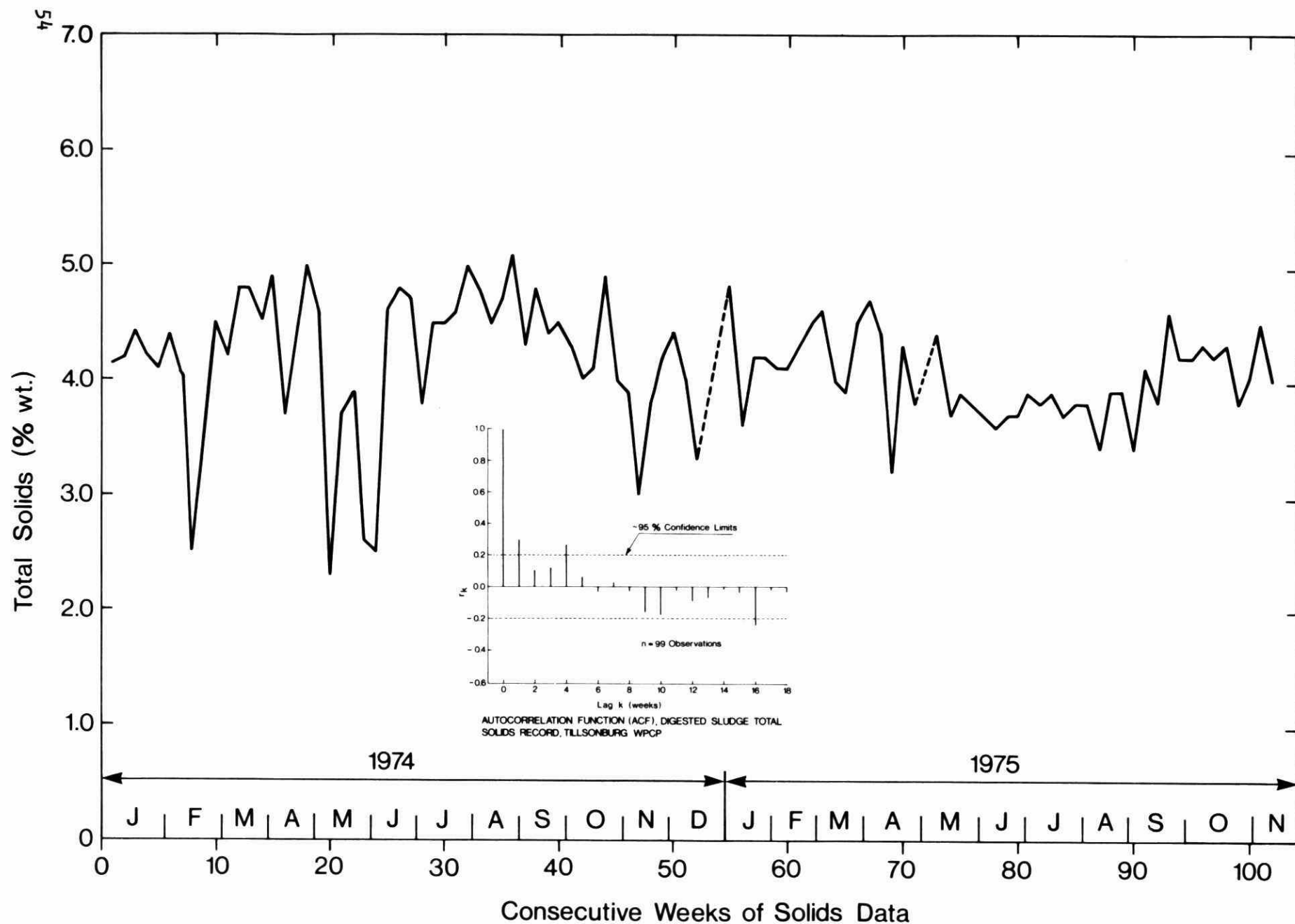
FIGURE 21. WEEKLY DIGESTED SLUDGE SOLIDS CONCENTRATIONS, TILLSONBURG WPCP, 1974-1975
(Dashed Lines Indicate Missing Data)

first, fourth, and sixteenth lags (Figure 21). The relatively small value of these correlation coefficients showed that the data were essentially random, deviating about a fixed mean. The random process does not restrict the sampling frequency here, and samples collected at weekly intervals will show no correlation (Adams and Gemmell, 1973; Bendat and Piersol, 1966). The sampling requirements are best obtained from an overall estimate of variability such as the RSD of a series of observations. This approach has been discussed in Section 4.6.2 and above.

It is suggested that improved within day sampling (Section 5) may significantly alter the process ACF at this plant. With continuous and uniform operation of the digestion system, including sludge discharge, one should expect significant autocorrelation in the series of observations. The random observations at this plant may be linked to the sampling and operating procedures within the plant, and may not reflect entirely the true process variations in sludge solids quality. For efficient and reliable sludge characterization, process monitoring, and process control, the importance of good sampling to overcome the limitations of the random type of sampling results produced here must be emphasized.

4.7   Effect of Variable Total Solids Concentrations

Comparison of heavy metals and total solids concentrations in the digested sludges at each of the five treatment plants suggested the existence of a relationship. Correlation by linear regression was used to check for a significant relationship between heavy metals (dependent variable) and total solids (independent variable). The correlation coefficients derived from the linear regressions for the short term sampling surveys are summarized in Table 12.

The majority of the correlations were strong. Whenever the concentration of a heavy metal was low the correlation coefficients were smaller. In this context, the "r" values for nickel were usually less than the values for other parameters.

TABLE 12. CORRELATION OF HEAVY METALS TO TOTAL SOLIDS IN
           DIGESTED SLUDGES

Heavy Metal	Correlation Coefficient, r				
	Simcoe	Chatham	Milton	Oakville S.E.	Tillsonburg
Fe	0.76	0.84	-	-	0.47
Al	0.76	0.81	-	-	0.83
Ni	0.39	0.72	0.75	0.93	0.15
Cu	0.89	0.78	0.97	0.97	0.88
Zn	0.56	0.79	0.98	0.95	0.96
Pb	0.87	0.88	0.96	0.95	0.52
Cd	0.85	0.50	-	-	0.70

        Total solids and heavy metals exhibited a strong correlation
at the Milton and Oakville WPCP's. Part of this was attributed to the
plants treating domestic sewage with little industrial input. Industries
can cause a great deal of heavy metal variability as discussed in
Section 5.2. Strong correlation between heavy metals and total solids
was observed with a highly variable total solids concentration. At
Milton total solids varied between 0.17 and 3.7% in the sludge hauled by
truck. The distribution of batch means at Milton is shown in Figure 22.
A limiting value on the order of 0.13 to 0.17% solids is the minimum
that can be expected at this plant due to total suspended solids and
total dissolved solids in the supernatant liquor. This supernatant was
observed in 16% of the 62 batches sampled; 40% of the batches had a mean
total solids concentration of less than 1% by weight. Supernatant
return from the digester to the plant is avoided because it reportedly
overloads the plant; consequently, digester supernatant is pumped into a
holding tank prior to hauling.

        In the short term sampling surveys, a high degree of correlation
was usually found between total solids and heavy metals. To test the
validity of correlating these variables over a longer period, linear
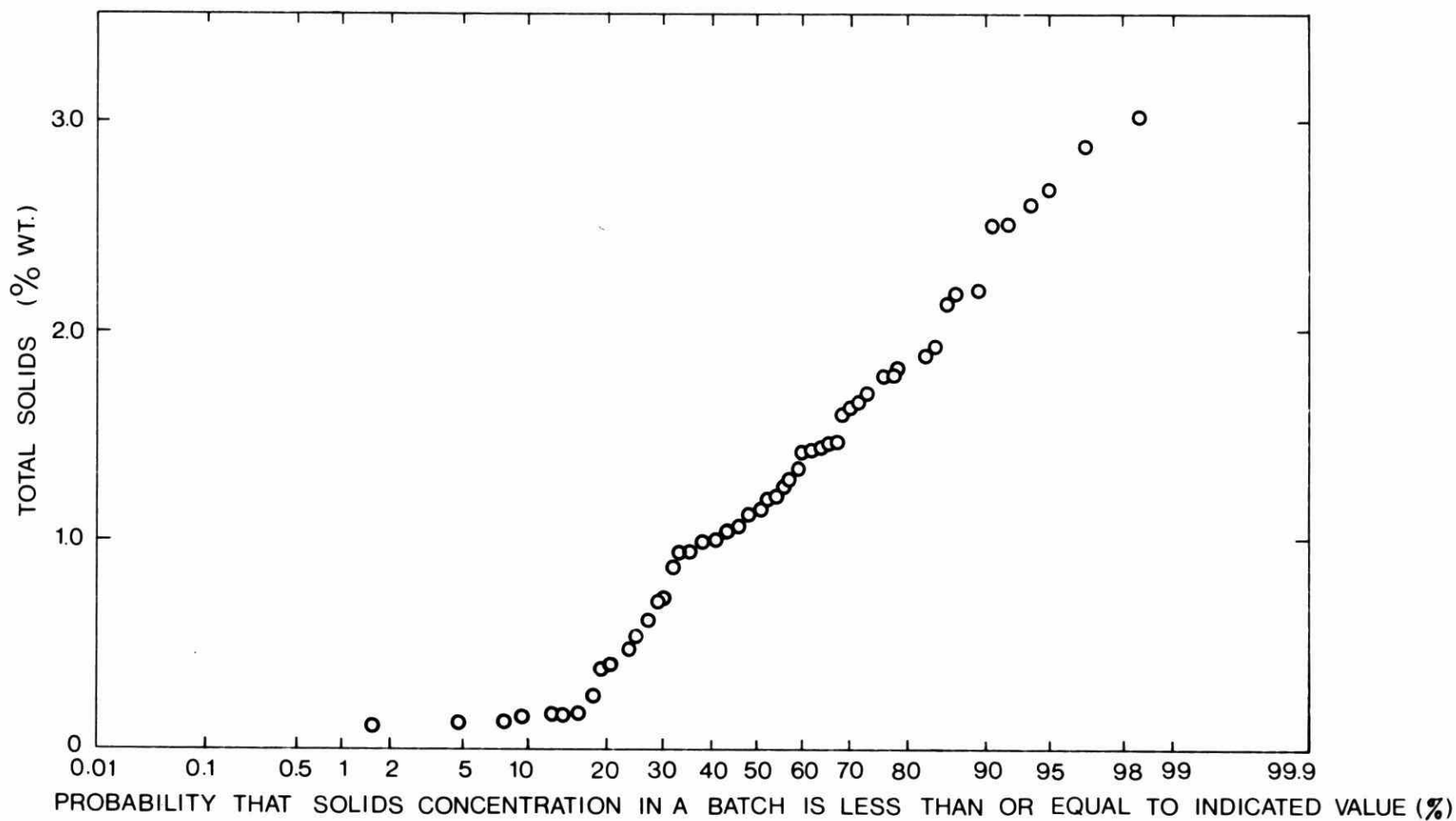
FIGURE 22. PROBABILITY DISTRIBUTION OF MEAN TOTAL SOLIDS CONCENTRATIONS IN BATCHES, MILTON WPCP

regression was carried out on the observations from the five-month study conducted at the Chatham plant. A lack of correlation was found for total solids with zinc and copper. From Figure 14 it is clear that copper had a peak concentration in August, while the maximum total solids concentration occurred in mid to late September. Zinc also had a peak concentration in August, but steadily increased in concentration after mid-September. This occurred while the total solids concentration in the sludge decreased after the peak food processing season.

The results indicate that, over a long period of time, correlation of digested sludge parameters cannot be expected. Problems associated with correlating passive data are discussed by Box (1966), and errors in estimating heavy metal concentrations from total solids could occur from its application. The linear regression equations could, perhaps, be used over a short period of time (about a month), but only with continual updating to account for changes in the sludge composition.

Because the heavy metal variability was related to total solids, conversion of the parameters from a wet weight to a dry weight basis reduced the overall variability. The RSD's of heavy metals decreased when recalculated on a dry weight basis (Table 4 and Appendix II). Liquid phase constituents such as NH_3-N and total dissolved solids were unaffected by conversions to a dry weight basis.

4.8 Residence Time Distribution Studies

4.8.1 Primary digester, Simcoe WPCP

The theoretical hydraulic detention time of the primary digester was calculated from daily raw sludge pumping records to be 35 days. A theoretical mixed flow model consisting of regions of bypass flow, backmix flow, and stagnation was fit by least squares techniques to the observed fluoride ion washout curve (Figure 23). The active backmix flow region, considered essential for digestion, was determined to be only 25% of the total fluid volume. Further, it was estimated that this region was effectively treating only 40% of the raw sludge

pumped to the digester with an observed residence time of 21.7 days. The remainder of the raw primary sludge was bypassing the active mixing region, and leaving the system within the first three days after entry. This condition was characterized by the series of high concentrations at $\theta = 0.06$ (Figure 23), the first sludge transfer day to the secondary digester after fluoride was introduced. The observations diminished in the order labelled "a, b, c" to the values labelled "d, e, f, g" on this day and, subsequently, followed a characteristic curve identifying a region of backmix flow (Figure 23). Measurements labelled "d, e, f, g" had the same values by coincidence. Clearly, a large proportion (75%) of the primary digester did not appear to be active in the digestion process. With improved mixing, it is probable that a more homogeneous sludge could be produced, particularly by dampening shock loads to the digestion process. The fluoride washout curve will be characteristic of any inert substance impulse to the system. An industrial discharge of a heavy metal would be a directly related example (Sections 4.6.1 and 4.8.4).

4.8.2   Secondary digester, Simcoe WPCP

Data from the fluoride ion washout curve indicated that the bulk of the tracer was discharged from the secondary digester within the first few hours after addition, though the theoretical residence time, based on the rate of sludge dewatered, was 29 days. This indicates that short circuiting was predominant when sludge was transferred with simultaneous centrifuge operation. Transferred sludge flowed directly to the withdrawal point in the secondary digester. Plant personnel also indicated sludge dewatering efficiency was reduced when sludge was transferred from the primary digester, usually in two increments each week. Each increment corresponded to an average of 15,000 Igal (68 m^3) during the study period. No further RTD studies were performed on the secondary digester; however, the available information indicates that improved operation could be anticipated by scheduling sludge transfer when centrifuging is not practised. This would produce additional benefits in terms of sludge homogeneity.
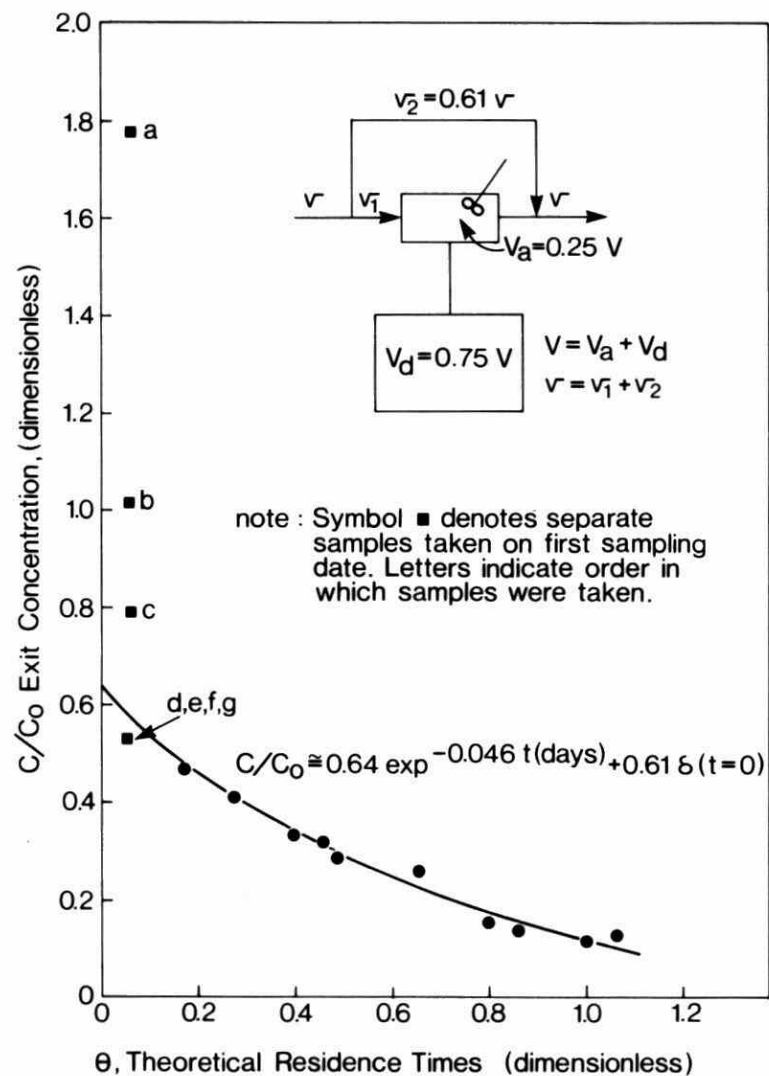
FIGURE 23. FLUORIDE TRACER WASHOUT CURVE, PRIMARY DIGESTER, SIMCOE WPCP

$v_2 = 0.61\ v$

$V_a = 0.25\ V$

$V_d = 0.75\ V$

$V = V_a + V_d$

$v = v_1 + v_2$

note : Symbol ■ denotes separate samples taken on first sampling date. Letters indicate order in which samples were taken.

$C/C_0 \cong 0.64\ \exp^{-0.046\ t\,(days)} + 0.61\ \delta\,(t=0)$
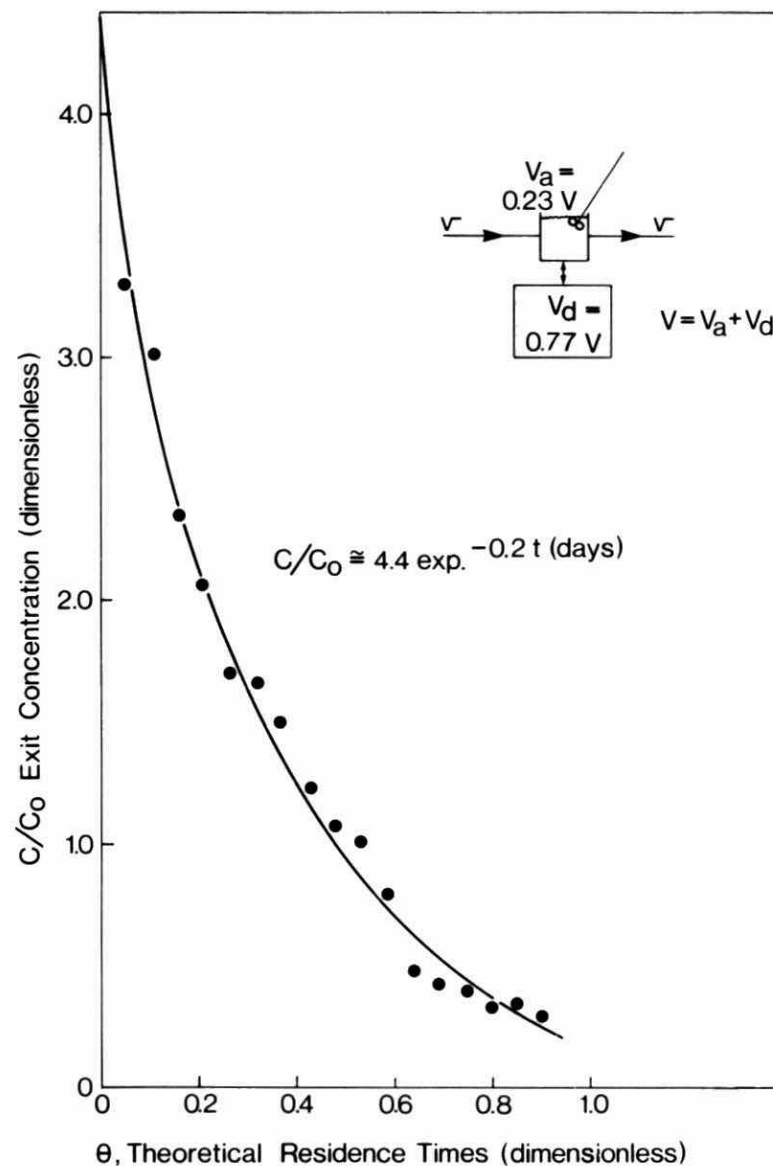
FIGURE 24. FLUORIDE TRACER WASHOUT CURVE, PRIMARY DIGESTER, CHATHAM WPCP

$V_a = 0.23\ V$

$V_d = 0.77\ V$

$V = V_a + V_d$

$C/C_0 \cong 4.4\ \exp^{-0.2\ t}\ (days)$

4.8.3 Primary digester, Chatham WPCP

The tracer response analysis indicated approximately 77% of the primary digester fluid volume was stagnant. The remaining volume (23%) was completely mixed with an observed mean residence time of 5.1 days based on the tracer data. No bypass flow was evident. The theoretical mean residence time of the primary digester was estimated to be 22.6 days based on the observed tracer washout curve (Figure 24), and 17.8 days based on sludge transfer rates to the secondary digester. The actual residence time (5.1 days) is unacceptable for standard rate digestion; however, 5.1 days is considered to be acceptable as a detention time when high rate anaerobic digestion is practised (Black, Crow and Eidsness, 1974). Shock loads such as heavy metal impulses would not be efficiently dampened by the poorly mixed system identified here. These loads will have a corresponding effect on the concentration discharged to the secondary digester. Section 4.8.4 illustrates this problem.

4.8.4 Secondary digester, Chatham WPCP

Seventy-eight percent of the secondary digester volume was actively mixed. The same percentage (78%) of the primary digester output entered into this region giving a mean residence time of 16.3 days. The remaining 22% of the primary digester output effectively bypassed the active mixing region, and flowed to the centrifuge within two or three days after entry to the secondary digester. The bypass flow time was interpreted from the peak concentration observed on the second operational day, $\theta \simeq 0.12$ (Figure 25). These calculations were based on a mean transfer rate of 28,300 Igal·day^{-1} (128 m^3·day^{-1}), and a total liquid volume of 459,000 Igal (2,080 m^3) in the secondary digester. The theoretical detention time for this system, treating the entire flow, was 16.2 days.

At the time of the study, this digester was mixed with product gas after completion of each day's run of the centrifuge. This procedure allegedly decreased the solids concentration on the tank bottom which was said to be detrimental to centrifuge operation. It cannot
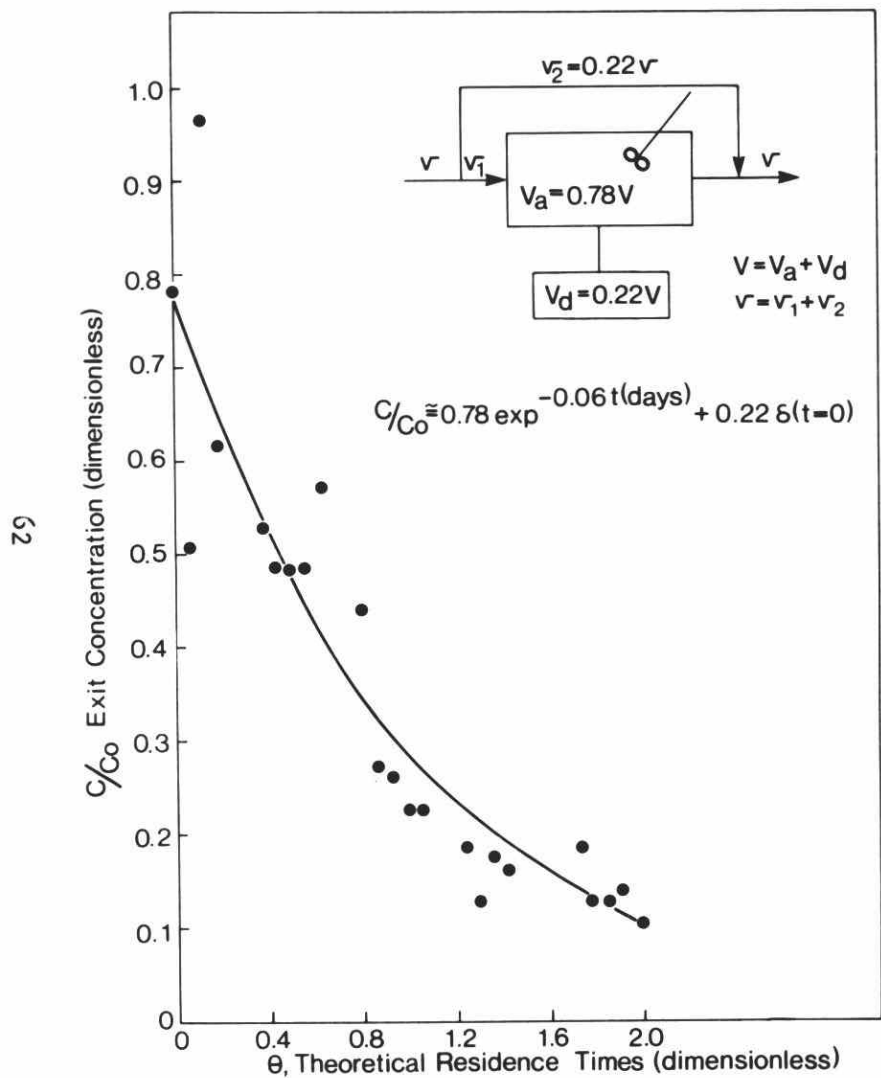
FIGURE 25. FLUORIDE TRACER WASHOUT CURVE, SECONDARY DIGESTER, CHATHAM WPCP

$$C/C_o \cong 0.78 \exp^{-0.06\,t\,(days)} + 0.22\,\delta(t=0)$$

$v_2 = 0.22\,v^-$

$V_a = 0.78V$

$V_d = 0.22V$

$V = V_a + V_d$

$v^- = v_1 + v_2$
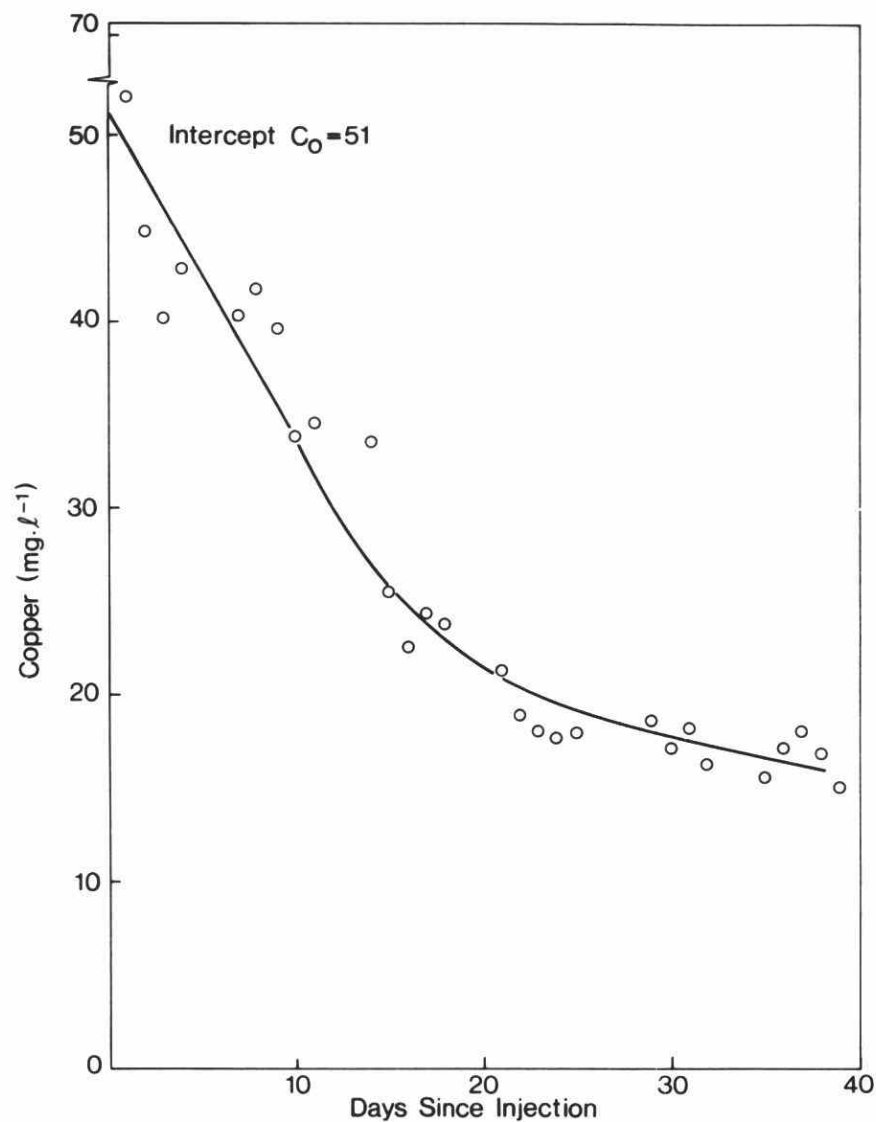
FIGURE 26. WASHOUT CURVE FOR OBSERVED COPPER SPIKE, SECONDARY DIGESTER, CHATHAM WPCP

Intercept $C_o = 51$

readily be explained why the secondary digester is better mixed than the primary; experimentation to characterize and optimize liquid and solid flow characteristics in anaerobic digestion systems would be useful. Additional studies may lead to an improvement of both the efficiency of these systems and the homogeneity of the end product, whether dewatering or liquid haulage is practised.

In August, 1975 simultaneous spikes of zinc and copper were observed in a series of secondary digested sludge samples (Section 4.6.1). The observed spikes decayed in a fashion similar to the fluoride washout curve. The pertinent copper washout curve has been replotted, and is shown in Figure 26. Assuming that the spike was instantaneous and described by a similar model used for the fluoride response, a mean residence time was determined to be about 12 days. In view of the assumptions, the agreement with the mean fluoride residence time (16.3 days) is good. The expected initial concentration, C_o, for the copper impulse was unknown; thus, the percentage stagnant volume could not be estimated. This is an excellent example of the system response under the influence of loads inefficiently damped by the primary digester. Such increases in heavy metal concentration are clear "fingerprints" of industrial discharges of the type described by Oliver and Cosgrove (1974). These dramatic and unpredictable changes impair the quality of the end product and its characterization.

4.9   Ammonia Electrode Studies

The results for the ammonia electrode evaluation were obtained as a three-factor experiment with replication. Analysis of variance techniques were used to assist in data interpretation (Table 13). The analysis indicated that the time factor (D) was the only significant source of variation. Neither the analysis technique nor the preparation method demonstrated any significant effects. In summary, the average NH_3-N concentration dropped from 1090 to 1010 mg$\cdot$l^{-1} during a three-day interval for the sample handled in this study. The apparent significance of the time factor was attributed to a loss of ammonia on standing. Three days intervened between the first and second preparation and

analysis steps, during which time the sample was held at room temperature. This observation indicates that sample handling may be an important factor in sampling sludge for ammonia determinations, and that rapid analysis will give a more accurate assessment of NH_3-N concentration in sludge destined for disposal.

TABLE 13.   ANALYSIS OF VARIANCE FOR COMPARISON OF SAMPLE
PREPARATION AND ELECTRODE TECHNIQUE

Source of Variation	df	SS	MS	F
Analysis Technique, A	1	253.50	253.50	<1
Time Factor, D	1	36,192.66	36,192.66	9.88
Preparation Method, B	2	2,970.33	1,485.17	<1
Replication, R	1	322.66	322.66	<1
Error	18	65,962.18	3,664.57	
TOTAL	23	105,701.33		

Since methods of sample preparation and analysis techniques were essentially the same, it was apparent that the preparation without filtering was most satisfactory because it was the least time consuming. Filtration, even of diluted sludge samples, took up to one hour per sample.   Dilution also reduces the concentrations of dissolved substances, grease, and organics which may affect ammonia solubility or shorten the electrode membrane life.

A separate data analysis was performed to evaluate differences between the electrode and the colourimetric automated procedure routinely used at the Wastewater Technology Centre.   Only filtered sample results were included in this data analysis, since a filtered sample is mandatory for the automated technique.   For the electrode response, the results of the preceding analysis were used, with additional results from automated analyses of the same samples.   All samples for automated analysis were stored and processed as a single batch; though prepared at two different times, these samples were stored for the same length of time.   Electrode

analyses were performed immediately after sample preparation. The analysis of the data (Table 14) revealed that two main factors, analysis technique (A) and time (D), yielded significant responses. Their interaction (A & D) was also significant. A summary of the significant effects is presented in Table 15. This summary shows a large drop in average NH_3-N concentration from D_1 to D_2, comprising a difference of 95 $mg \cdot l^{-1}$, or about a -10% change. This effect was also referred to in the preceding analysis. The significant response among the A factors was unexpected; comparison of the A means using the standard error (± 26 $mg \cdot l^{-1}$) showed that A_3 was different than both A_1 and A_2. The interaction means (A and D) with standard error of ± 36 $mg \cdot l^{-1}$ indicate that, on D_1, A_3 was different than A_1, but not A_2. On D_2, however, A_3 was 90 $mg \cdot l^{-1}$ less than A_1 and A_2. It was believed that a longer storage time before automated analysis was responsible for this decrease.

TABLE 14. ANALYSIS OF VARIANCE FOR COMPARISON OF ELECTRODE
RESPONSE TO COLOURIMETRIC RESPONSE

Source of Variation	df	SS	MS	F
Analysis Technique, A	2	27,827.08	13,913.54	26.9
Time Factor, D	1	55,104.16	55,104.16	106.7
Interaction, A & D	2	85,908.33	42,954.17	83.2
Preparation Method, B	1	337.50	337.50	<1
Replication, R	1	4.16	4.16	<1
Error	16	8,264.60	516.54	
TOTAL	23	177,445.83		

TABLE 15. TREATMENT MEANS FOR COMPARISON OF ELECTRODE
AND COLOURIMETRIC TECHNIQUE*

	D_1		D_2	Mean	
A_1	1120		1020	1070	
A_2	1085	(± 36)	1020	1050	(± 26)
A_3	1050		930	990	
Mean	1085	(± 21)	990		

* All results in mg·l^{-1}.
A_1 Known addition.
A_2 Calibration.
A_3 Colourimetric.
D_1 Day 1.
D_2 Day 2.

For the second part of this study, an electrode was provided
to the staff at the Chatham WPCP. A laboratory technician was instructed
to operate the electrode using the known addition technique of analysis
on unfiltered, diluted samples of digested sludge. From June 23 to
August 29, 1975, 45 samples were collected and analyzed at the plant
site. This permitted assessment of electrode performance in the field,
and during a longer time than the initial part of the study. To provide
a control, these 45 samples were refrigerated and sent to the Wastewater
Technology Centre on a weekly basis and prepared for automated colouri-
metric analysis. The paired data were used to detect differences in
reproducibility arising from analytical technique, or from other sources
of variation such as sample handling or preparation. Table 16 summarizes
the results of this comparison. On the average, the electrode response
was about 17 ± 8 mg·l^{-1} (9 to 25 mg·l^{-1}) greater than the response of the
colourimetric technique. The reproducibility is adequate at this con-
centration level for most practical purposes. Other studies at the
Wastewater Technology Centre have indicated that ammonia losses as great
as 50 to 180 mg·l^{-1} may occur during sludge sample filtration. Sludge

pH values were observed to increase from 7.0 to 7.4 in the slurry to 8.4 in the filtrate of some samples. In addition to the effect of the vacuum during filtration, this pH change was thought to be responsible for the stripping of ammonia from the sample. These changes in concentration did not occur consistently; pH should be monitored carefully in sludge samples before and after filtration. The problem associated with sludge filtration and delays in sample analysis favour the use of the electrode for routine NH_3-N analyses. The technique is rapid, and a filtered sample is unnecessary. Both these factors may lead to more accurate results.

TABLE 16. COMPARISON OF FIELD EVALUATION OF AMMONIA ELECTRODE
           WITH LABORATORY COLOURIMETRIC TECHNIQUE

	Electrode	Colourimetric
Mean $(mg \cdot l^{-1})$	547	534
$\bar{d} \pm$ 95% CL $(mg \cdot l^{-1})$	17±8	

The known addition technique was advantageous because it eliminated the need for standardizing solutions and calibration curves. Known addition is the preferred technique for samples containing high and variable quantities of dissolved species (Orion Research, 1974).

Plant personnel measuring ammonia in sludge samples remarked that determinations were easy, fast, and not inconvenient compared to other routine laboratory tests.

5   GENERAL DISCUSSION

5.1   Variability of Digested Sludges Within Days

The most striking observation in this study dealing with
variability was the decrease of total solids content in sludges with-
drawn from a digester within a day. The decrease of other constituent
concentrations was linked to this effect. It was also apparent that
increasing rates of sludge withdrawal resulted in increasing variability
in constituent concentrations. This is based on the observation that
treatment plants disposing sludge by tank truck produced a sludge with
greater variability than plants dewatering sludge on a semi-continuous
basis. A volume of sludge dewatered in three or four hours may, equiva-
lently, be pumped to a tank truck in about one-tenth of the time. The
largest differences were observed between batches of sludge hauled
within a day; differences between samples within days at dewatering
plants were smaller. The components of variance for each parameter
indicated that variations between days were not statistically signifi-
cant at plants hauling sludge by truck; at plants which dewatered
sludge, the component of variance between days frequently contributed
the least amount to variability.

Based on the estimate of variance, s^2, for "within days" or
"within batches" variability, the relative standard deviation, RSD, of
the mean parameter concentrations at each plant were estimated
(Table 17). These RSD estimates can be used to predict the obtainable
precision in mean concentrations for a given sample size (Figure I-1,
Appendix I). For a sample size, n=3, obtainable precisions in mean
concentrations are tabulated in Table 18 for given RSD's (Table 17).
These estimates reflect the difference between plants dewatering sludge
(Simcoe, Chatham) and plants disposing sludge by tank truck (Milton,
Oakville). Also, the heterogeneity of solid phase constituents (Zn,
TKN) is contrasted with liquid phase constituents (NH_3-N). It is apparent
that a reasonable sample size, say n=3, can be expected to give a wide
range in the degree of precision in mean constituent concentrations. At
plants which dispose liquid sludge, the within batch precision can vary
in the range ±7 to ±55% of the mean depending on the constituent of

interest. This range relates to separate, batch truck loads of digested sludge. At plants which dewatered sludge, the within day precision ranged from ±5 to ±16% of the means. The higher degree of precision here is believed to be related to the rate of sludge withdrawal from the digester, and to reduced channeling in the sludge blanket.

TABLE 17. WITHIN DAY RSD's (%) AND WITHIN BATCH RSD's (%) AT FOUR WATER POLLUTION CONTROL PLANTS*

		Constituents			
	Plant	TS	Zn	NH_3-N	TKN
Within Days	Simcoe	9	10	4	7
	Chatham	14	14	4	11
Within Batches	Milton	37	48	16	40
	Oakville S.E.	37	40	6	23

$$* \text{ RSD (\%)} = \frac{100 \sqrt{s_0^2 + s_1^2}}{\bar{x}}$$

s_0^2 = Component of variance between repeats within samples.

s_1^2 = Component of variance between samples within batches, or between samples within days.

Rather than employing a relatively complex sampling plan devised by an allocation procedure (Section 1-2, Appendix 1), a one-day sampling program with a periodicity of two weeks is recommended to characterize all constituents. In Section 4.6.2, the RSD for one year's record of digested sludge solids was calculated to be ±22%. If 26

sludge samples were collected annually, the estimated precision of the annual mean solids concentration would be about ±10% for this RSD of 22% (Figure I-1, Appendix I). Thus, if one sample is collected every two weeks, the same precision is maintained as in the allocation procedure (Table 4). A RSD of ±22 to ±25% for sludge variability is a reasonable estimate in the light of the values found by Thomann (1970) for other process streams at sewage treatment plants. Time series analysis of long term records from one plant (Chatham), where significant system responses were obtained and where mixing studies were performed to characterize detention times, indicated that a two-week sampling frequency (i.e., one sampling day every two weeks) was adequate to account for long term variations. Inspection of Figure 14 shows that this frequency should be adequate to account for changes in other constituent concentrations also.

TABLE 18. OBTAINABLE PRECISIONS (±%) IN MEAN PARAMETER CONCENTRATIONS FOR SAMPLE SIZE n = 3

		Parameter			
	Plant	TS	Zn	NH_3-N	TKN
Within Days	Simcoe	10	12	5	8
	Chatham	16	16	5	13
Within Batches	Milton	43	55	18	46
	Oakville S.E.	43	46	7	27

Since within day variability is highly significant, it is important to obtain a representative sample during a sampling day. Where sludge is discharged semi-continuously to dewatering devices, it is recommended that a composite sample, composed of at least three grab

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samples collected through an operating day, be obtained for effective sludge characterization. Constituent concentrations on non-sampling days should be estimated from concentrations measured on the nearest sampling day. Again, indications are that a two-week sampling frequency is adequate to account for long term changes in sludge quality. The estimated precision of parameter concentrations then should be in the range ±5 to ±16% at plants that dewater sludge (Simcoe, Chatham). This is based on the results presented in Table 18; the actual value depends on the constituent of interest. Each composite is designed to account for the observed decrease of the sludge solids concentration during a day.

Where sludge is discharged batchwise it is clear that batches of sludge must be sampled and analyzed separately on a sampling day for effective characterization. At least three grab samples should be systematically collected and composited for each batch load. Constituent concentrations in batches discharged on a non-sampling day should be estimated by results from corresponding batches on the nearest sampling day. For each hauling day, the mean parameter concentrations within a given batch can be estimated with a precision in the approximate range ±7 to ±55%, depending on the parameter of interest. A frequency of one sampling day every two weeks should be adequate to account for long term variations.

Table 19 summarizes the digested sludge sampling recommendations which have been formulated from this study, and gives a side-by-side comparison for batch and semi-continuous modes of sludge withdrawal. Also, Figure I-1 (Appendix I), Table 17, and a two-week sampling frequency have been used to re-evaluate the sample collection procedures necessary to obtain an arbitrarily stipulated precision (±25%) in mean total solids concentration for both withdrawal modes; the results are given in Table 19. This re-evaluation clearly shows the greater effort required to characterize sludges from batch mode plants with a precision equivalent to that obtainable at semi-continuous mode plants, and demonstrates the flexibility which can be obtained in a sampling scheme by using Figure I-1.

TABLE 19. SUMMARY OF SAMPLING PLANS FOR CHARACTERIZATION OF DIGESTED SLUDGES

WPCP Type	Sampling Frequency	Sample Collection	Precision* (±%)			
			Total Solids	Zinc	TKN	NH₃-N
Semi-Continuous Mode (e.g., de-watering plant)	$\frac{1 \text{ day}}{14 \text{ days}}$	3 grab samples composited to make one sample	16	16	13	5
	$\frac{1 \text{ day}}{14 \text{ days}}$	2 grab samples composited to make one sample**	25	25	20	7
Batch Mode (e.g., truck haulage to farm land)	$\frac{1 \text{ day}}{14 \text{ days}}$	3 grab samples per batch composited to make one sample; each batch sampled separately	43	46	27	7
	$\frac{1 \text{ day}}{14 \text{ days}}$	9 grab samples per batch composited to make one sample; each batch sampled separately	25	27	15	4

* Precisions estimated at 95% confidence level.
** Nearest whole number of samples required to obtain stipulated precision.

A well founded sampling strategy is essential to characterize process streams efficiently. The plans described here provide a sound basis for sampling strategies to characterize digested sludges as they are currently processed.

5.2   Heavy Metal Variability

A high degree of correlation was noted between total solids and heavy metals in the short term. The data of Sommers et al. (1973) suggested similar results in digested sludges from ten Indiana cities. Their analyses of sludge filtrates showed that, essentially, all metals were retained in the filter cakes; the correlation of heavy metals and

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total solids resulted in the metals having RSD's of a magnitude similar to the RSD for total solids. Consequently, when metal concentrations were expressed on a dry weight basis, the number of samples required for characterization was reduced by eliminating the effect of solids variability.

A study of total solids and heavy metal concentrations over a period of several months (Section 4.6.1) revealed that linear correlations were not valid when applied over the long term. Increases in solids and heavy metal concentrations were independent, resulting in a lack of correlation, and the series of heavy metal observations were characterized by shifting means. Although the regression equations may be useful for a short time, by necessity they would have to be continually updated and modified to account for changing metal concentrations.

It is not too surprising that metals vary considerably in digested sludge. Abbott (1971) found that metal concentrations in raw sewage were highly variable, and often exceeded sewer by-laws. Oliver and Cosgrove (1974) sampled intensively at a sewage treatment plant. Among their observations were the following:

1.   metal input was not a continuous process, but consisted of slugs of metals lasting for a discrete time;
2.   several metals had coincident curves, indicating they arose from the same sources; and,
3.   the slugs of metals did not occur periodically and could not be predicted.

These points emphasize the randomness of the metal input, and help indicate why digested sludges, the sink for many metals in sewage treatment plants, may show large fluctuations in heavy metal concentrations. The slugs of metals are damped out to some extent by the large volume of sludge in the digesters, but variability with time is still a problem. When pollution control plants record heavy metal concentrations in digested sludge, the total solids concentration for the sample should also be recorded. In this way, an increase in heavy metals in sludge might be attributed to a corresponding increase in total solids; otherwise, the metal concentrations might be attributed to

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a breach of sewer by-laws, or at least derivation from a new source. Regular monitoring of digested sludges for heavy metal concentrations can help to identify when metals are rising to undesirable levels, and to indicate the magnitude of the variability that can be expected for individual plants.

5.3   Control of Sludge Variability

Much of the variability in digested sludge composition could be reduced if the digesters were operated efficiently. Control of the anaerobic digestion process is an area where there is much room for improvement. The use of control charts (Zickefoose and Hayes, 1976) might be considered as one means of monitoring operation with, as an example, control based on the total solids concentrations in the digested sludge. The system would indicate "out of control" situations when the solids concentration rises above or drops below predetermined levels. At the high end, the sludge may contain excessive heavy metal concentrations; a sludge low in solids may be uneconomical to haul or dewater. An example of the application of control charts to water pollution control is given by Berthouex and Hunter (1975). An introduction to their use is presented in a 1972 EPA publication (Analytical Quality Control Laboratory, 1972).

Residence time distribution studies conducted during the project indicated that inefficient mixing was a problem in the digesters. Better mixing can improve the operating efficiency of a digester and dampen pulses to the system, resulting in better homogeneity of the end product. Long term records at two plants were examined to determine whether any relationship existed between raw and digested sludge solids. The resulting cross correlation function (CCF) revealed that raw sludge solids were significantly correlated to digested sludge solids at one plant. This is evidence that one cannot expect a uniform end product with variable input even though digestion systems are characterized by long detention times.

In 1947, Schlenz observed "the design and operation of sludge digestion systems has not been given the consideration it deserves", and "digestion tanks have been operated as a 'take-up' in the sewage treatment process to accommodate the optimum schedules of other portions of the system, without regard to the maintenance of proper conditions for digestion". Nearly 30 years later, these statements are still relevant. Visits to various water pollution control plants have shown that plant records such as raw sludge pumping rates or digester gas production have occasionally been neglected. Plants should be encouraged to maintain complete records. Data should be recorded in meaningful, exact terms to facilitate future interpretation and use. Time of sampling, location of sampling, batch number, and other concurrent process factors are some examples of conditions which must be reported to produce useful information. This study showed the importance of time of sampling or batch number as significant factors in monitoring sludge. It is doubtful that supportive data such as these are provided at the majority of WPCP's. In addition, the digestion system frequently appears to be run as a "black box" with no real control over the process or the quality of the digested sludge. Recent studies (Graef and Andrews, 1974; Silveston Engineers, 1974) have used computer simulation to model digesters with the aim of optimizing performance. These developments hold promise for better operation of digesters.

Instrumentation is an area where improvement could be made. Plant operators complained about raw sludge meters and gas meters working improperly. These devices are susceptible to the action of corrosive compounds, and should be designed with this in mind. Gas production is one of the most important operating parameters to be monitored in digestion, but it is neglected in many cases. Special instruments have been developed for anaerobic sludge monitoring. These include a deep water minimum-maximum thermometer for temperature profiles in digesters, a sludge sampling bathometer to obtain a solids profile in the digester, and a portable level measuring device for determining sludge blanket levels in secondary digesters (Dimovski, 1970).

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This project showed that the solids concentration in sludge decreases while a truck is being filled, or when a dewatering device is operated. For truck haulage, the economics of semi-continuous sludge withdrawal to a sludge solids hopper may outweigh the costs of haulage of dilute slurry to land disposal sites; also, the product variability would be reduced significantly. A sludge density meter such as that proposed by Garrison and Nagel (1959) may be used to activate or switch pumps if the sludge solids concentration falls below a pre-determined level. Where the sludge is withdrawn from one of several sumps in a digester floor, a density meter could switch sludge withdrawal from one sump to another as it detects a decrease in the sludge density.

Adoption of control strategies for optimizing anaerobic digesters (e.g., scrubbing CO_2 from digester gas with subsequent gas recycle, addition of a base, recycling digested sludge (Graef and Andrews, 1974)) should be considered. Additional reduction in solids and increased gas production have been realized with digested solids recycle (Torpey and Melbinger, 1967; Pfeffer, 1968). Use of electrode potentials for monitoring the digestion process and electrolysis for process control (Blanc and Molof, 1973) might also be considered in order to prevent upsets during adverse loading conditions. Use of instrumentation can help achieve a more constant sludge solids concentration, reducing variability and the sample size needed for characterization.

5.4   Ammonia Electrode

The ammonia electrode can be used at a sewage treatment plant where regulations require monitoring of sludges and effluents. The electrode can provide an accurate, fast evaluation of ammonia concentration at the plant site.

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REFERENCES

1. Abbott, R.A., <u>Metals in Municipal Sewerage Systems</u>, Division of Industrial Wastes, Ontario Water Resources Commission, 1971.

2. Adams, B.J. and R.S. Gemmell, "Performance of Regionally Related Wastewater Treatment Plants", <u>Journal Water Pollution Control Federation</u>, <u>45</u>(10):2088, 1973.

3. American Public Health Association, American Water Works Association, Water Pollution Control Federation, <u>Standard Methods for the Examination of Water and Wastewater</u> (13th Ed.), APHA-AWWA-WPCF, Washington, D.C., 1971.

4. Analytical Quality Control Laboratory, <u>Handbook for Analytical Quality Control in Water and Wastewater Laboratories</u>, United States Environmental Protection Agency, Cincinnati, Ohio, 1972.

5. Laboratory Services Section, <u>Analytical Methods Manual</u>, <u>Wastewater Technology Centre</u>, Wastewater Technology Centre, Environmental Protection Service, Burlington, Ontario, 1976.

6. Anderson, M.S., "Comparative Analyses of Sewage Sludges", <u>Sewage and Industrial Wastes</u>, <u>28</u>(2):132, 1956.

7. Arnold, J.C., "A Markovian Sampling Policy Applied to Water Quality Monitoring of Streams", <u>Biometrics</u>, <u>28</u>(4):739, 1970.

8. Bates, T.D., "Disposal of Sewage Sludge on Land", <u>Proceedings Technical Seminar on Sewage Sludges - Conditioning, Dewatering and Disposal</u>, Toronto, Ontario, November 16, Ontario Ministry of the Environment and the Pollution Control Association of Ontario, 1972.

9.   Bates, T.D., J.R. Moyer and A. Haq, "Effects of Sewage Sludge on
        Crop Growth and Nutrient and Metal Uptake", Sludge Handling and
        Disposal Seminar, Canada-Ontario Agreement Conference Proceedings
        No. 2, Toronto, Ontario, September 18-19, Environment Canada and
        Ontario Ministry of the Environment, 1974.

10.   Beauchamp, E.G. and J. Moyer, "Nitrogen Transformation and
        Uptake", Sludge Handling and Disposal Seminar, Canada-Ontario
        Agreement Conference Proceedings No. 2, Toronto, Ontario, September
        18-19, Environment Canada and Ontario Ministry of the Environment,
        1974.

11.   Bendat, J.S. and A.G. Piersol, The Measurement and Analysis of
        Random Data, John Wiley and Sons, New York, 1966.

12.   Berrow, M.L. and J. Webber, "Trace Elements in Sewage Sludges",
        Journal Science of Food and Agriculture, 23(1):93, 1972.

13.   Berthouex, P.M. and W.G. Hunter, "Treatment Plant Monitoring
        Programs: a Preliminary Analysis", Journal Water Pollution
        Control Federation, 47(8):2143, 1975.

14.   Bingham, F.T., A.L. Page, R.J. Mahler and T.J. Ganje, "Growth
        and Cadmium Accumulation of Plants Grown on a Soil Treated with
        a Cadmium-Enriched Sewage Sludge", Journal of Environmental
        Quality, 4(2):207, 1975.

15.   Black, Crow and Eidsness, Consulting Engineers, "Process Design
        Manual for Sludge Treatment and Disposal", United States
        Environmental Protection Agency, 1974, (EPA 625/1-74-006).

16.   Black, S.A., "Land Application of Sewage Sludge", Technology
        Transfer Seminar on Alternatives for Nutrient Control, Kelowna,
        British Columbia, October 29-31, Environmental Protection Service
        and Pollution Control Branch of the B.C. Water Resources Service,
        1975.

17.   Blanc, F.C. and A.J. Molof, "Electrode Potential Monitoring and Electrolytic Control in Anaerobic Digestion", Journal Water Pollution Control Federation, 45(4):655, 1973.

18.   Boswell, F.C., "Municipal Sewage Sludge and Selected Element Applications to Soil: Effects on Soil and Fescue", Journal of Environmental Quality, 4(2):267, 1975.

19.   Box, G.E.P., "The Use and Abuse of Regression", Technometrics, 8(4):625, 1966.

20.   Box, G.E.P. and G.M. Jenkins, Time Series Analysis, Forecasting and Control, Holden-Day, San Francisco, 1970.

21.   Bradford, G.R., A.L. Page, L.J. Lund and W. Olmstead, "Trace Element Concentrations of Sewage Treatment Plant Effluents and Sludges: Their Interactions with Soils and Uptake by Plants", Journal of Environmental Quality, 4(1):123, 1975.

22.   Burd, R.S., "A Study of Sludge Handling and Disposal", United States Department of the Interior, Federal Water Pollution Control Association, Washington, D.C., 1968. (Publication WP-20-4)

23.   Chawla, V.K., J.P. Stephenson and D. Liu, "Biochemical Characteristics of Digested Chemical Sewage Sludges", Sludge Handling and Disposal Seminar, Canada-Ontario Agreement Conference Proceedings No. 2, Toronto, Ontario, September 18-19, Environment Canada and Ontario Ministry of the Environment, 1974.

24.   Cholette, A. and L. Cloutier, "Mixing Efficiency Determinations for Continuous Flow Systems", Canadian Journal of Chemical Engineering, 37:105, 1959.

25.   Davies, O.L. (ed.), <u>The Design and Analysis of Industrial</u>
        <u>Experiments</u>, 2nd ed., Oliver and Boyd (for Imperial Chemical
        Industries Ltd.), London, 1956.

26.   Davies, O.L. and P.L. Goldsmith (ed.), <u>Statistical Methods in</u>
        <u>Research and Production</u>, 4th ed., Hafner Publishing Co., (for
        Imperial Chemical Industries Ltd.), New York, 1972.

27.   DiLallo, R. and O.E. Albertson, "Volatile Acids by Direct
        Titration", <u>Journal Water Pollution Control Federation</u>, <u>33</u>(4):356,
        1961.

28.   Dimovski, K.L., "Some Devices Required in the Operation of
        Equipment for the Anaerobic Treatment of Sludges of Domestic
        and Industrial Wastewaters", <u>Trud. Nauchnoizsled. Inst. Vodosnab.</u>
        <u>Kanaliz Sanit. Tek., Sofia</u>, (Bulgarian) <u>5</u>:115-123, 1970.

29.   Dowdy, R.H. and W.E. Larson, "The Availability of Sludge-Borne
        Metals to Various Vegetable Crops", <u>Journal of Environmental</u>
        <u>Quality</u>, <u>4</u>(2):278, 1975a.

30.   Dowdy, R.H. and W.E. Larson, "Metal Uptake by Barley Seedlings
        Grown on Soils Amended with Sewage Sludge", <u>Journal of</u>
        <u>Environmental Quality</u>, <u>4</u>(2):229, 1975b.

31.   Ewing, B.B. and R.I. Dick, "Disposal of Sludge on Land", in
        <u>Water Quality Improvement by Physical and Chemical Processes</u>,
        edited by E.F. Gloyna and W.W. Eckenfelder Jr., University of
        Texas Press, Austin, Texas, 1970.

32.   Garrison, W.E. and C.A. Nagel, "A Density Meter to Control
        Sludge Pumping", <u>Sewage and Industrial Wastes</u>, <u>31</u>(11):1327, 1959.

33.   Graef, S.P. and J.F. Andrews, "Stability and Control of Anaerobic
        Digestion", _Journal Water Pollution Control Federation_, 46(4):666,
        1974.

34.   Gross, M.G., "Preliminary Analyses of Urban Wastes, New York
        Metropolitan Region", Marine Sciences Research Center, State
        University of New York, Stony Brook, New York, 1970 (Technical
        Report No. 8).

35.   Hodges, P.B., "Unique Sampling and Flow Measurement Devices for
        In-plant Waste Control", _Proceedings, 14th Industrial Waste
        Conference_, Purdue University, West Lafayette, Indiana, May 5-7,
        1959.   (Engineering Extension Series No. 104)

36.   Kelly, J.C. and D.A. McManus, "Optimizing Sediment Sampling
        Plans", _Marine Geology_, 7(5):465, 1969.

37.   Kendall, M.G., _Rank Correlation Methods_, 4th ed., Hafner
        Publishing Co., New York, 1970.

38.   Kennewell, J. and N. Long, "An Evaluation of New Methods for the
        Determination of Ammonia in Water", in _Examination of Waters:
        Evaluation of Methods for Selected Characteristics_, compiled by
        J.A. McGlynn, Australian Government Publishing Service, Canberra,
        1974.   (Australian Water Resources Council Technical Paper No.
        8)

39.   Klee, A.J. and D. Carruth, "Sample Weights in Solid Waste
        Composition Studies", _Journal Sanitary Engineering Division,
        American Society of Civil Engineers_, 96(SA4):945, 1970.

40.   Klein, L.A., M. Lang, N. Nash and S.L. Kirschner, "Sources of
        Metals in New York City Wastewater", _Journal Water Pollution
        Control Federation_, 46(12):2653, 1974.

41.   Knopp, P.V., "Frequency Response Analysis of the Activated
        Sludge Process", Ph.D. thesis, Department of Engineering,
        University of Wisconsin, Madison, 1967.

42.   Law, J.P., "Agricultural Utilization of Sewage Effluent and
        Sludge: an Annotated Bibliography", United States Department
        of the Interior, Federal Water Pollution Control Administration,
        Washington, D.C., 1968. (Report GWR-2)

43.   LeBlanc, P.J. and J.F. Sliwinski, "Specific Ion Electrode of
        Ammonium Nitrogen in Waste Waters", American Laboratory,
        5(7):51, 1973.

44.   Levenspiel, O., Chemical Reaction Engineering, 2nd ed., Wiley,
        New York, 1972.

45.   Loffell, B.L. "Some Studies on the Movement of Sludge Within a
        Digestion Tank during the Digestion Process", Public Health,
        Johannesburg, 18(9):29, and 18(10):10, 1955.

46.   Manson, R.J. and C.A. Merritt, "Farming and Municipal Sludge:
        They're Compatible", Compost Science, 16(4):16, 1975.

47.   McQuaker, N.R., "The Determination of Fluoride by the Specific
        Ion Electrode Method", in A Laboratory Manual for the Chemical
        Analysis of Waters, Wastewaters and Biological Tissues, Chemistry
        Laboratory, Water Resources Services, Department of Lands,
        Forests and Water Resources, Province of British Columbia, 1973.

48.   Montgomery, H.A.C. and I.C. Hart, "The Design of Sampling
        Programmes for Rivers and Effluents", Water Pollution Control,
        73(1):77, 1974.

49.   Mortvedt, J.J. and P.M. Giordano, "Response of Corn to Zinc and
        Chromium in Municipal Waters Applied to Soil", Journal of
        Environmental Quality, 4(2):170, 1975.

50.   Novotny, V. and R.M. Stein, "Equalization of Time Variable Waste
        Loads", Journal of the Environmental Engineering Division, ASCE,
        102(EE3):613, 1976.

51.   Oden, S., B. Berggren and A.G. Engvall, "Heavy Metals and
        Chlorinated Hydrocarbons in Sludge", Grundfforbattring (Swedish),
        23(5):55, 1970.

52.   Oliver, B.G. and E.G. Cosgrove, "The Efficiency of Heavy Metal
        Removal by a Conventional Activated Sludge Treatment Plant",
        Water Research, 8(11):869, 1974.

53.   Orion Research, Instruction Manual, Fluoride Electrode Model
        96-09, Orion Research Inc., Cambridge, Massachusetts, 1973.

54.   Orion Research, Instruction Manual, Ammonia Electrode Model
        95-10, Orion Research Inc., Cambridge, Massachusetts, 1974.

55.   Petersen, R.G. and L.D. Calvin, "Sampling", in Methods of Soil
        Analysis: Volume 1. Physical and Mineralogical Properties,
        edited by C.A. Black, American Society of Agronomy, Madison,
        Wisconsin, 1965.

56.   Peterson, J.R., C. Lue-Hing and D.R. Zenz, "Chemical and
        Biological Quality of Municipal Sludge", Symposium on Recycling
        Treated Municipal Wastewater and Sludge Through Forest and
        Cropland, University Park, Pennsylvania, August 22, Pennsylvania
        State University, 1972.

57.   Pfeffer, J.T., "Increased Loadings on Digesters with Recycle of
        Digested Solids", Journal Water Pollution Control Federation,
        40(11):1920, 1968.

58.   Ryan, J.A. and D.R. Keeney, "Ammonia Volatilization from Surface-Applied Wastewater Sludge", Journal Water Pollution Control Federation, 47(2):386, 1975.

59.   Sabey, B.R. and W.E. Hart, "Land Application of Sewage Sludge: 1. Effect on Growth and Chemical Composition of Plants", Journal of Environmental Quality, 4(2):252, 1975.

60.   Schlenz, H.F., "Important Considerations in Sludge Digestion. Part 1 - Practical Aspects", Sewage Works Journal, 19(1):19, 1947.

61.   Silveston, B. and P., Engineers, Notes for Workshop on Computer-Aided Design and Simulation of Waste Treatment Systems, Environment Canada, Ottawa, 1974. (Environmental Protection Service Report No. EPS 6-WP-74-1)

62.   Snedecor, G.W. and W.G. Cochran, Statistical Methods, 6th ed., Iowa State University Press, Ames, Iowa, 1967.

63.   Sommers, L.E., D.W. Nelson, J.E. Vahner and J.V. Mannering, "Chemical Composition of Sewage Sludge from Selected Indiana Cities", Purdue University Agricultural Experiment Station Journal Paper No. 4957, Lafayette, Indiana, 1973.

64.   Tenney, M.W. and G.J. Budzin, "How Good is Your Mixing?", Water and Wastes Engineering, 9(5):57, 1972.

65.   Thomann, R.W., "Variability of Waste Treatment Plant Performance", Journal Sanitary Engineering Division, ASCE, 96(SA3):819, 1970.

66.   Thomas, R.F. and R.L. Booth, "Selective Electrode Measurement of Ammonia in Water and Wastes", Environmental Science and Technology, 7(6):523, 1973.

67. Torpey, W.N. and N.R. Melbinger, "Reduction of Digested Sludge Volume by Controlled Recirculation", _Journal Water Pollution Control Federation_, _39_(9):1464, 1967.

68. Van Loon, J.C., J. Lichwa, O. Ruttan and J. Kinrade, "The Determination of Heavy Metals in Domestic Sewage Treatment Plants", _Water, Air and Soil Pollution_, _2_(4):473, 1973.

69. Verhoff, F.H., M.W. Tenney and W.F. Echelberger, Jr., "Mixing in Anaerobic Digestion", _Biotechnology and Bioengineering_, _16_(6):757, 1974.

70. Wallace, A.T. and D.M. Zollman, "Characterization of Time-Varying Organic Loads", _Journal Sanitary Engineering Division, ASCE_, _97_(SA3):257, 1971.

71. Webber, J., "Effects of Toxic Metals in Sewage on Crops", _Water Pollution Control_, _71_(4):404, 1972.

72. Zickefoose, C. and R.B. Hayes, "Operational Manual Anaerobic Sludge Digestion", United States Environmental Protection Agency, 1976. (EPA 430/9-76-001)

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APPENDIX I

SUMMARY OF DATA ANALYSES METHODS

UNBALANCED ANOVA FOR SAMPLES WITHIN SAMPLES

At the Milton and Oakville S.E. WPCP's, the data fit an
unbalanced experimental design since (i) samples were replicated randomly,
and (ii) the number of truck loads of sludge hauled in any single day
varied. An example of a typical sampling schedule for the Milton WPCP
is shown in Table I-1. This schedule covers a one-week interval. The
details of calculations involved in estimating the components of variance
are described in detail by Snedecor and Cochran (1967) on page 291;
however, an example of the resultant calculations for TKN is shown for
the Oakville S.E. WPCP (Table I-2).

TABLE I-1. TYPICAL SAMPLING WEEK, MILTON WPCP*

Batch \ Day	Monday	Tuesday	Wednesday	Thursday	Friday
1	1 2 3	1R 2R 3	1 2R 3R	No Hauling	1R 2 3
2	1R 2R 3R	1 2 3	1R 2 3		1R 2 3R
3	1 2 3R				1 2 3R

* Numbers in boxes represent sample number in batch; a
  number followed by 'R' indicates that a replicate sample
  was collected.

TABLE I-2. ANOVA FOR TKN, OAKVILLE S.E. WPCP

	Level 0 Between Repeats Within Samples	Level 1 Between Samples Within Batches	Level 2 Between Batches Within Days	Level 3 Between Days	Level 4 Total
C_i*	147	99	33	8	1
SS_i**	994,726,500	989,899,100	965,494,880	939,331,400	930,537,570

* C_i = number of classes in level i.
** SS_i = sum of squares of level i.

VALUES OF AUXILIARY QUANTITIES γ_{ij} and k_{ij}

i \ j	γ_{ij} 0	1	2	3	4
4	1	1.65	4.70	19.72	147
3	8	13.24	37.62	147	
2	33	51.90	147		
1	99	147			
0	147				

i \ j	k_{ij} 0	1	2	3
3	7	11.59	32.92	127.3
2	25	38.66	109.4	
1	66	95.10		
0	48			

TABLE I-2.   ANOVA FOR TKN, OAKVILLE S.E. WPCP (Continued)

Source of Variation	df	Sum of Squares	Mean Square	Expected Value of Mean Square
Between days (level 3)	7	8,793,830	1,256,260	$\sigma_0^2 + 1.66\sigma_1^2 + 4.70\sigma_2^2 + 18.2\sigma_3^2$
Between batches within days (level 2)	25	26,163,480	1,046,540	$\sigma_0^2 + 1.55\sigma_1^2 + 4.38\sigma_2^2$
Between samples within batches (level 1)	66	24,404,220	369,760	$\sigma_0^2 + 1.44\sigma_1^2$
Between repeats within samples (level 0)	48	4,827,400	100,570	σ_0^2

The components of variance can be estimated from the expected mean squares:

$$s_0^2 = 100,570$$
$$s_1^2 = 186,940$$
$$s_2^2 = 149,820$$
$$s_3^2 = 7,770$$

OPTIMUM SAMPLING ALLOCATION

Allocation of sampling can be determined using "optimum allocation of sampling resources". This method is outlined in detail by Snedecor and Cochran (1967) and Davies (1956). Sampling allocation is optimized using a balance between (i) cost of sampling and (ii) variations in samples.

In the first step the designated precision is related to the variance of the mean:

$$\ell\bar{x} \quad = \quad t\sqrt{Var\ \bar{x}} \tag{4}$$

where t =   value of t-distribution for (n-1) d.f. at 95% confidence level ≈ 2.

Var $\bar{x}$ =   measured variance of mean.

Once Var $\bar{x}$ has been determined for any constituent, it can be related to the components of variance:

$$Var\ \bar{x} \quad = \quad \frac{s_3^2}{n_3} + \frac{s_2^2}{n_2 n_3} + \frac{s_1^2}{n_1 n_2 n_3} + \frac{s_0^2}{n_0 n_1 n_2 n_3} \tag{5}$$

with s_i^2 =   component of variance for effect i,
$0 \leq i \leq 3$ (effects may be batch, hour, day, etc.).

n_i =   sample size determined for effect i.

Included within the n_i is a balance between costs and components of variation:

$$n_i \quad = \quad \sqrt{\frac{c_{i+1}}{c_i} \cdot \frac{s_i^2}{s_{i+1}^2}} \tag{6}$$

where c_i =   cost related to sampling for effect i.

When k effects are examined, Equation (6) is used to calculate n_0, n_1 ...n_{k-1}, and Equation (5) is used to solve for n_k.

Costs were estimated by considering the samples to have been collected by the plant operators. The first cost ratio established was the cost of physically taking several samples compared to the cost of analysis. Since analysis of samples can be very expensive (e.g., $20 to $25 per single analysis of one sample). the cost of sampling is usually much less than the cost of analysis. Thus, cost of sampling/cost of analysis $\ll 1$, and n_0 (number of replicate analyses) is set equal to one. Although n_0 might be considerably less than one, the minimum sample collected must be an integral number.

Similarly, other cost ratios were established. In considering the cost of collecting many samples in a few batches, or a small number of samples in many batches, the operator's time was considered. Since he is continually at the sampling site, the amount of time the operator needs to sample frequently on one or two days, or a few times on many days, will be nearly equal. Consequently, all cost ratios were assumed to be approximately one. These were estimates but, since the cost ratios are within a square root term (Equation 6), the sensitivity to the cost ratio is decreased considerably.

The sampling allocation for TKN at Oakville S.E. illustrates the procedure:

$$\bar{x} = 2540 \text{ mg} \cdot l^{-1}$$

$$\text{Let precision of mean} = 0.10 \, \bar{x}$$
$$= 0.10 \, (2540)$$
$$= 254$$
$$= t \sqrt{\text{Var } \bar{x}}$$
$$2 \sqrt{\text{Var } \bar{x}} = 254$$
$$\therefore \text{Var } \bar{x} = 16,129$$

$$\frac{c_1}{c_0} = \frac{\text{cost of sampling}}{\text{cost of analysis}} \simeq 1 \qquad \therefore n_0 = 1 = \text{no. of replicates}$$

$$\frac{c_2}{c_1} = \frac{\text{cost of sampling more batches}}{\text{cost of collecting more samples per batch}} \simeq 1$$

$$\frac{c_3}{c_2} = \frac{\text{cost of sampling more days}}{\text{cost of sampling more batches per day}} \simeq 1$$

From the ANOVA for TKN in Oakville S.E. sludge,

$$s_0^2 = 100{,}570 = \text{component due to repeats}$$

$$s_1^2 = 186{,}940 = \text{component due to samples}$$

$$s_2^2 = 149{,}820 = \text{component due to batches}$$

$$s_3^2 = 7{,}780 = \text{component due to days}$$

∴ the number of samples/batch,

$$n_1 = \sqrt{\frac{c_2}{c_1} \cdot \frac{s_1^2}{s_2^2}} = \sqrt{\frac{186{,}940}{149{,}820}} = 1.12 \text{ or } n_1 \simeq 1.$$

and the number of batches/day,

$$n_2 = \sqrt{\frac{c_3}{c_2} \cdot \frac{s_2^2}{s_3^2}} = \sqrt{\frac{149{,}820}{7{,}700}} = 4.39 \text{ or } n_2 \simeq 4.$$

and since $\text{Var } \bar{x} = \dfrac{s_3^2}{n_3} + \dfrac{s_2^2}{n_2 n_3} + \dfrac{s_1^2}{n_1 n_2 n_3} + \dfrac{s_0^2}{n_0 n_1 n_2 n_3}$

then $16{,}129 = \dfrac{7{,}770}{n_3} + \dfrac{149{,}820}{4 n_3} + \dfrac{186{,}940}{4(1) \cdot n_3} + \dfrac{100{,}570}{4(1) \cdot (1) n_3}$

and solving for the number of days, $n_3 = 7.26$ or $n_3 \simeq 7$. The rounding to integral numbers reduces the precision of the mean slightly.

$$\text{Total} = n_0 n_1 n_2 n_3 = 1 \times 1 \times 4 \times 7 = 28 \text{ samples.}$$

If the precision of the mean is relaxed to $\pm 0.25 \bar{x}$,
$\text{Var } \bar{x} = 100{,}800$ and $n_3 = 1.16$ or $n_3 \simeq 1.$

It is important to note that the numbers estimated by this method are the optimum number of samples for the given costs, variabilities, and stipulated precisions. Any changes in the constraints will tend to increase the total number of samples from the optimum. Consider, for example, a situation in which samples can be taken only on two days and four batch loads of sludge are removed each day. How many samples per batch must be collected for an allowable error of $\pm\,0.10\,\bar{x}$? Using Equation (6) to determine n_1,

$$16,129 = \frac{7,770}{2} + \frac{149,820}{2(4)} + \frac{186,940}{2(4)n_1} + \frac{100,570}{2(4)(1)n_1}$$

$$\therefore\ n_1 = 3.87\ \text{ or }\ n_1 \simeq 4.$$

Departure from the optimum sampling allocation in this case increases the total number of samples required from 28 to 32.

I-3   SAMPLE SIZE PLOT

Sample size may be estimated assuming an approximately normal distribution of the sample mean. The expression defining sample size is:

$$n = 4(s)^2/L^2 \tag{1}$$

where n = estimate of required sample size to obtain $\bar{x} \pm L$

L = allowable error in sample mean = $\ell\bar{x}$

ℓ = stipulated precision of mean $\bar{x}$, $0<\ell<1$ for the purposes of this analysis

Equation (1) can be rewritten as:

$$n = 4(s)^2/(\ell\bar{x})^2 \tag{2}$$

and since RSD = 100 $s/\bar{x}$, Equation (2) can be rewritten as:

$$n = 4\left(\frac{RSD}{100}\right)^2 \Big/ \ell^2 \tag{3}$$

A family of curves can be developed from this Equation (Figure I-1).
When the RSD of the mean has been calculated, and the precision of the
mean has been stipulated, the required sample size can be determined
readily from Figure I-1. As noted in the body of the report, the sample
size plot indicates how many samples are needed, but not the sampling
allocation, which is at least as important.
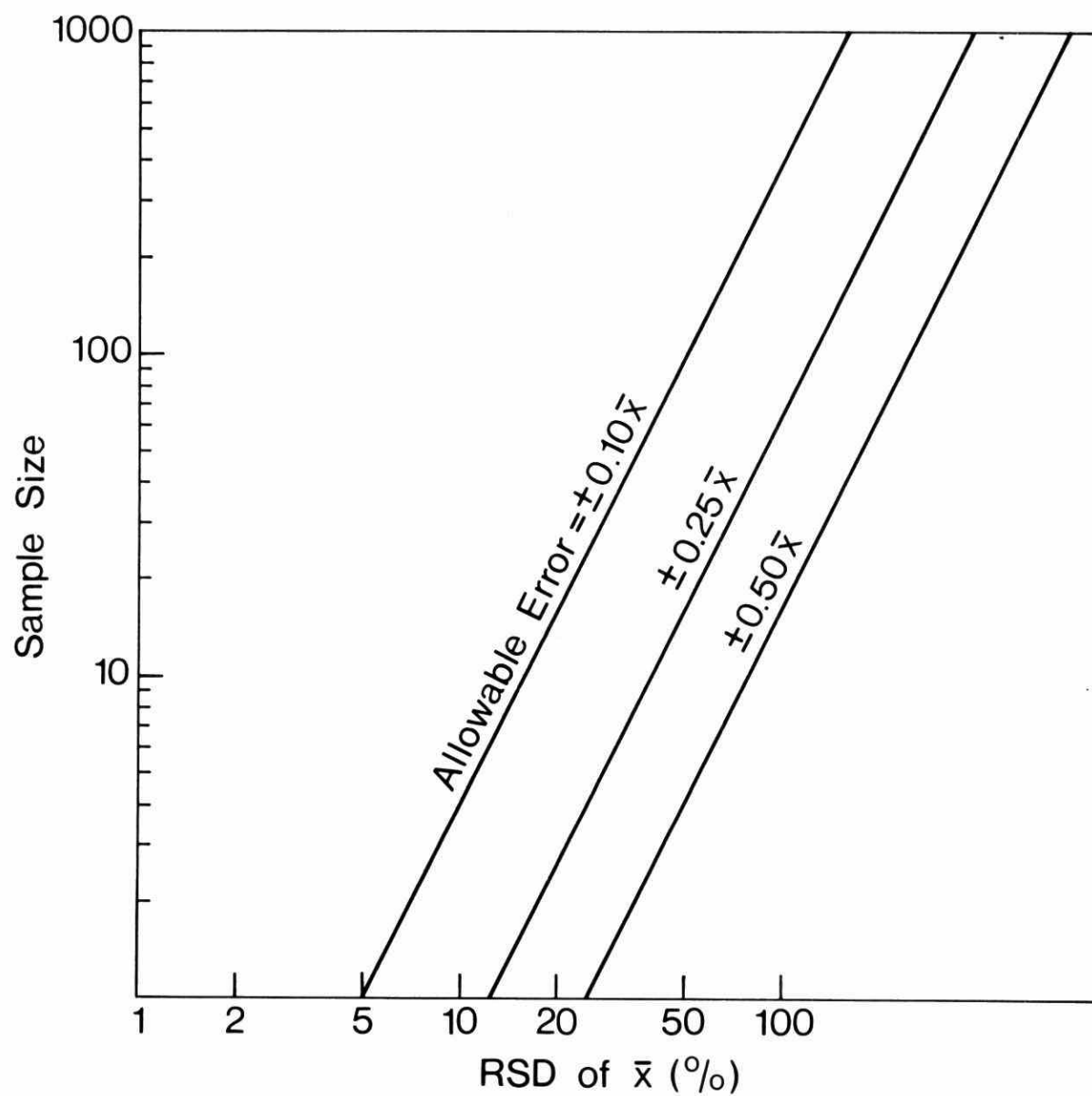
FIGURE I-1 SAMPLE SIZE DETERMINATION PLOT

APPENDIX II

DATA SUMMARY

TABLE II-1. STATISTICAL SUMMARY OF PARAMETERS IN DIGESTED SLUDGES, MILTON
AND OAKVILLE S.E. WPCP

WPCP	Parameter	Grand Mean $(mg \cdot l^{-1})$	Sample Standard Deviation $(mg \cdot l^{-1})$	RSD (%)	95% CL of Mean $(mg \cdot l^{-1})$	Range of Parameter $(mg \cdot l^{-1})$	RSD Dry Wt. Basis (%)
Milton	VS	6,080	4,330	71.2	620	410-17,600	11.0
	Ni	0.36	0.33	92	0.05	0.01-1.50	52
	Cu	7.7	5.9	77	0.9	0.10-23.1	46
	Pb	3.7	3.2	87	0.5	0.01-16.2	53
Oakville S.E.	VS	17,300	6,460	37.4	1,000	2,900-34,300	8.70
	Ni	1.06	0.47	44.0	0.10	0.15-2.80	19.4
	Cu	30.0	13.2	43.9	2.6	4.7-64.0	9.44
	Pb	22.0	10.5	48.0	2.1	2.9-60.0	14.8

TABLE II-1. STATISTICAL SUMMARY OF PARAMETERS IN DIGESTED SLUDGE, CHATHAM WPCP

WPCP	Parameter	Grand Mean $(mg \cdot l^{-1})$	Sample Standard Deviation $(mg \cdot l^{-1})$	RSD (%)	95% CL of Mean $(mg \cdot l^{-1})$	Range of Parameter $(mg \cdot l^{-1})$	RSD Dry Wt. Basis (%)
Chatham	Total P	986	263	26.7	34	290-1,730	19.5
	TOC	5,750	962	16.7	130	3,120-8,000	7.81
	Vol. Solids	15,400	2,400	15.6	300	9,740-20,300	4.88
	TDS	1,170	156	13.4	50	840-1,570	-
	pH	7.3	0.1	1.2	-	7.0-7.4	-
	Fe	3,060	570	18.6	70	1,900-4,630	9.96
	Al	840	132	15.7	20	545-1,510	9.76
	Ni	5.2	1.0	19	0.1	2.8-8.4	14
	Cu	16.0	3.3	20.6	0.4	9.6-23.6	13.5
	Pb	18.0	3.2	16.9	0.4	12.2-28.0	8.69
	Cd	0.10	0.068	68	0.01	0-0.4	52

TABLE II-1. STATISTICAL SUMMARY OF PARAMETERS IN DIGESTED SLUDGE, SIMCOE WPCP

WPCP	Parameter	Grand Mean $(mg \cdot l^{-1})$	Sample Standard Deviation $(mg \cdot l^{-1})$	RSD (%)	95% CL of Mean $(mg \cdot l^{-1})$	Range of Parameter $(mg \cdot l^{-1})$	RSD Dry Wt. Basis (%)
Simcoe	Total P	411	82.5	20.1	12	200-680	15.2
	TOC	6,640	703	10.6	100	5,380-9,780	6.80
	VS	15,300	1,400	9.15	200	11,800-19,400	5.44
	TDS	1,520	277	18.2	40	720-2,160	-
	pH	7.54	0.17	2.25	0.02	7.10-8.00	-
	Fe	3,880	554	14.3	80	2,680-5,840	9.43
	Al	142	20.9	14.8	3	98-212	9.84
	Ni	1.12	0.34	30.4	0.05	0.60-3.30	31.2
	Cu	18.8	2.1	11.2	0.3	16.4-26.2	5.17
	Pb	14.6	1.8	12.2	0.3	12.8-21.6	6.20
	Cd	2.51	0.30	12.0	0.04	2.10-3.60	5.98

TABLE II-1. STATISTICAL SUMMARY OF PARAMETERS IN DIGESTED SLUDGES, TILLSONBURG WPCP

WPCP	Parameter	Grand Mean $(mg \cdot l^{-1})$	Sample Standard Deviation $(mg \cdot l^{-1})$	RSD (%)	95% CL of Mean $(mg \cdot l^{-1})$	Range of Parameter $(mg \cdot l^{-1})$	RSD Dry Wt. Basis (%)
Tillson-burg	Total P	2,410	571	23.7	180	1,120-3,340	25.6
	TOC	8,980	849	9.45	270	7,790-11,000	4.58
	VS	21,800	1,700	7.80	540	18,700-24,900	3.61
	TDS	958	64.2	6.70	21	835-1,080	-
	pH	7.55	0.12	1.56	0.04	7.3-7.8	-
	Fe	409	68.6	16.8	22	292-620	14.5
	Al	2,360	209	8.86	67	1,940-2,740	5.19
	Ni	0.98	0.17	18	0.06	0.70-1.50	18
	Cu	37.5	3.1	8.24	1.0	32.0-44.8	3.97
	Pb	9.7	0.88	9.0	0.3	8.40-12.0	8.4
	Cd	0.38	0.050	13	0.02	0.28-0.52	9.6

APPENDIX III

FREQUENCY DISTRIBUTIONS OF PARAMETERS IN
FIVE DIGESTED SLUDGES

SIMCOE SLUDGE   AUG 19 – SEPT 3 , 1974

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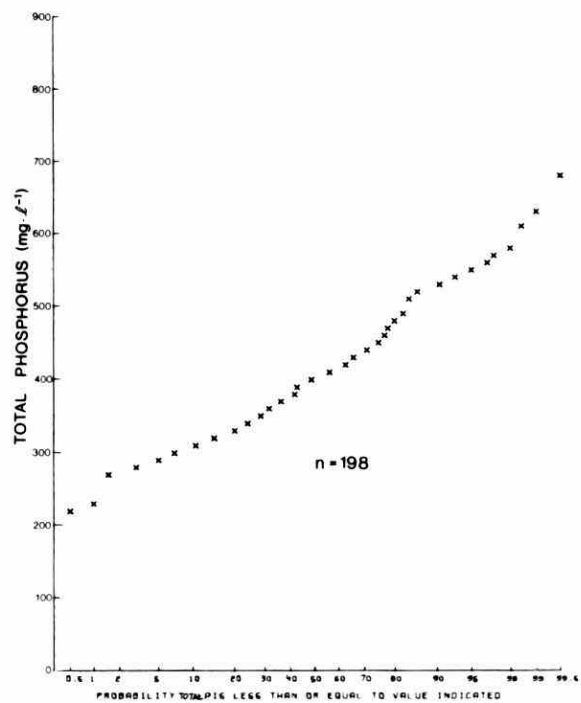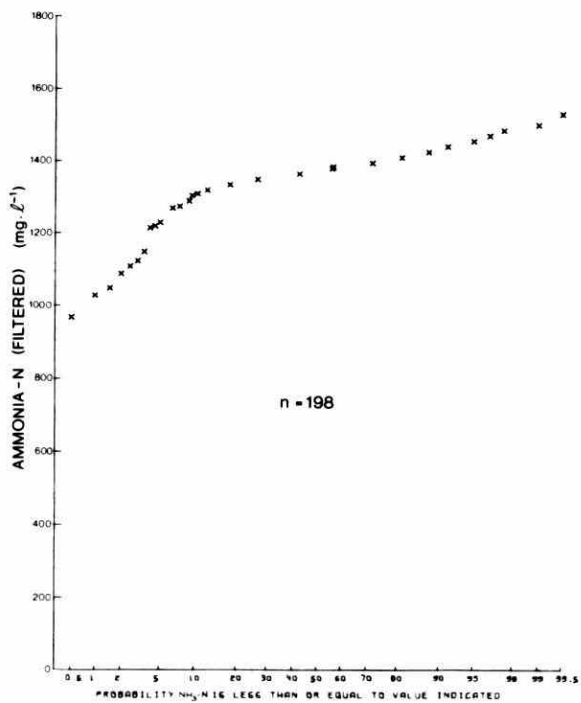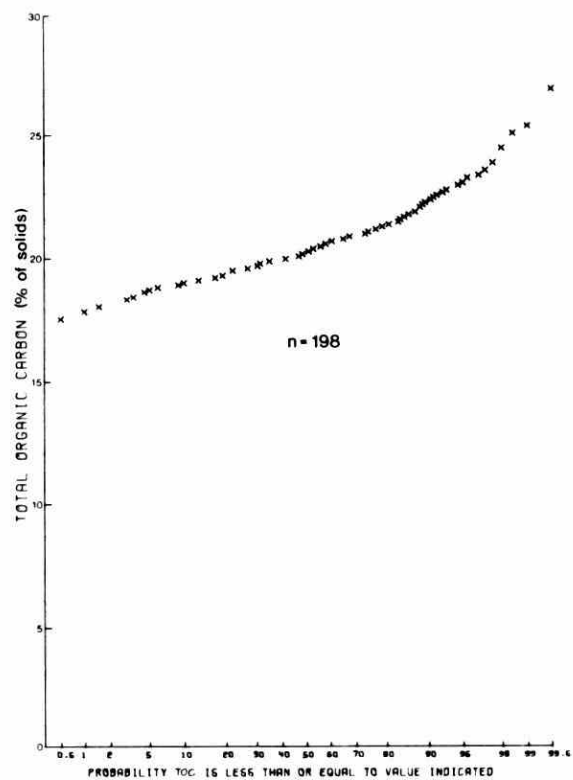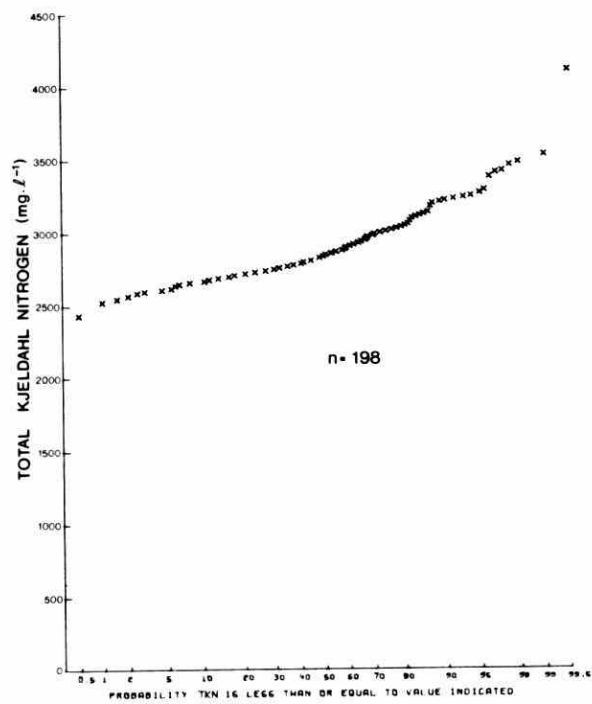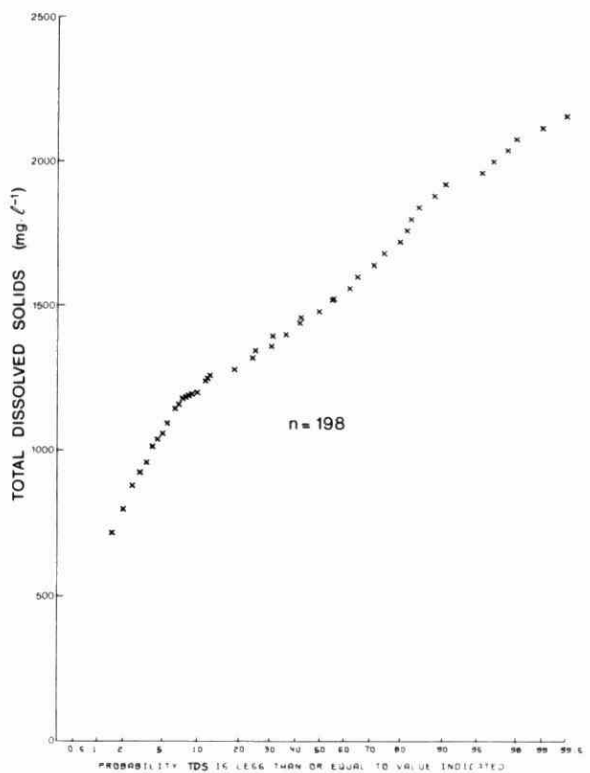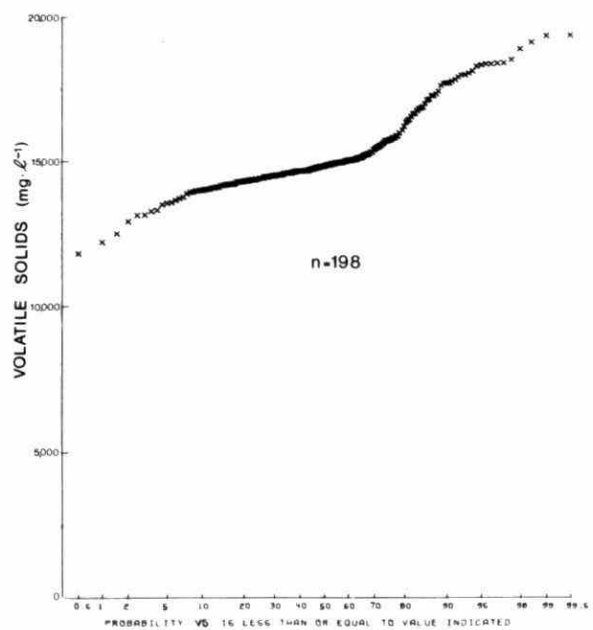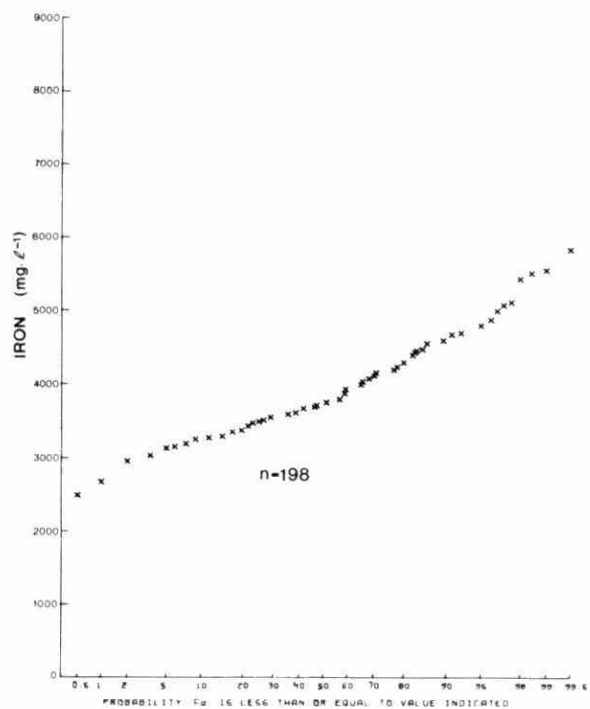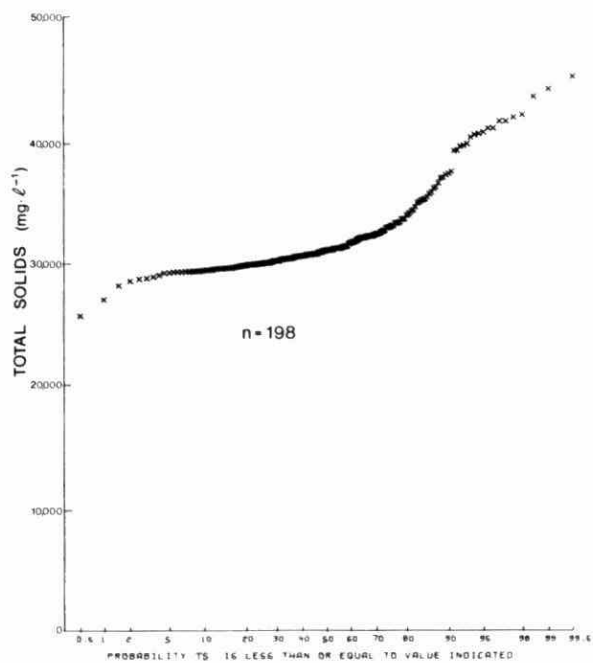
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SIMCOE SLUDGE   AUG 19 – SEPT 3, 1974

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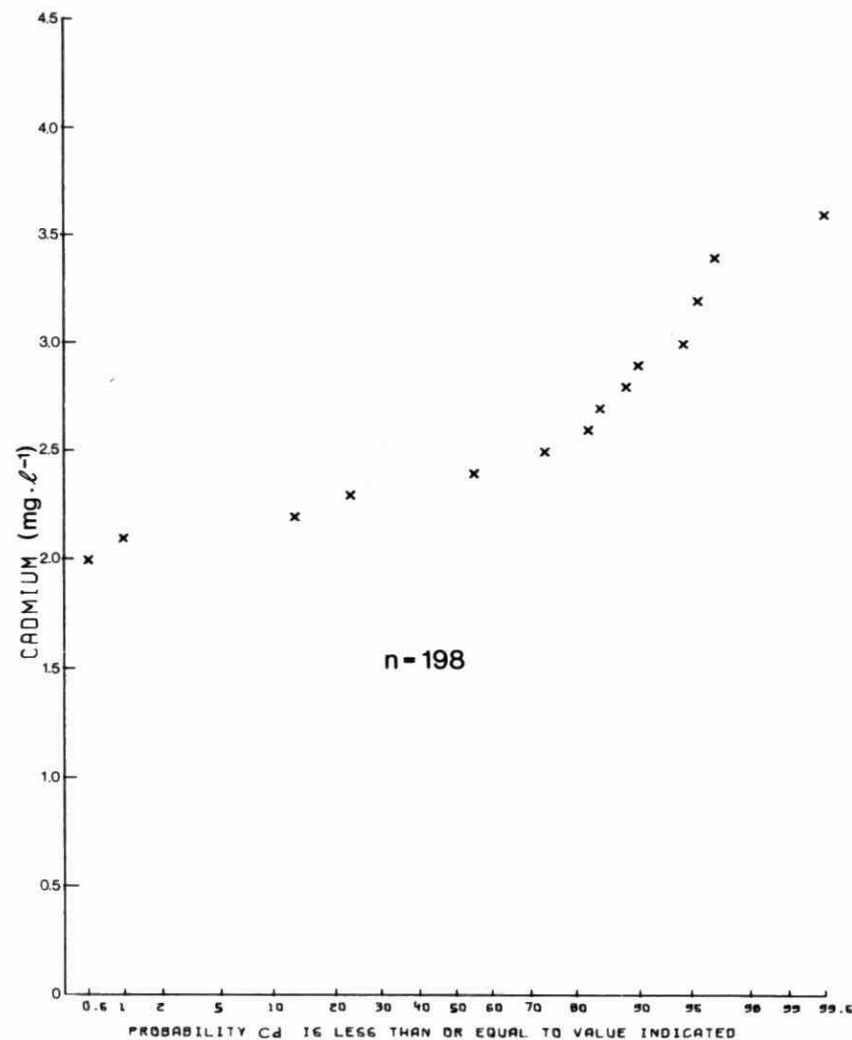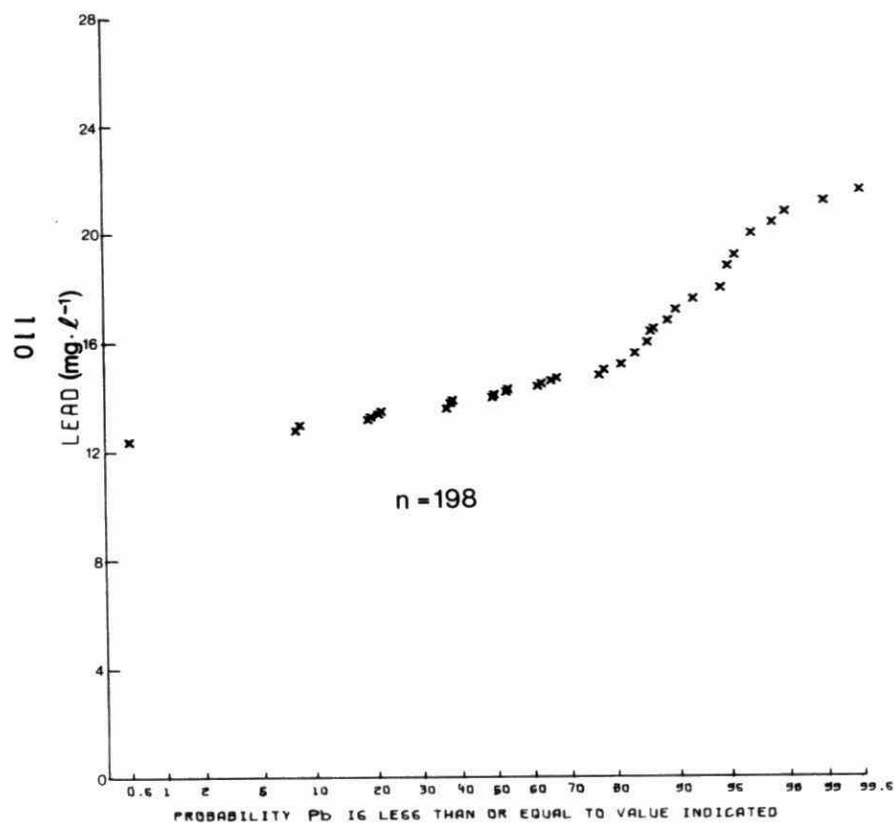
SIMCOE SLUDGE   AUG. 19 – SEPT. 3, 1974

CHATHAM SLUDGE   MARCH 3-21, 1975

111

CHATHAM   SLUDGE   MARCH 3–21, 1975

112
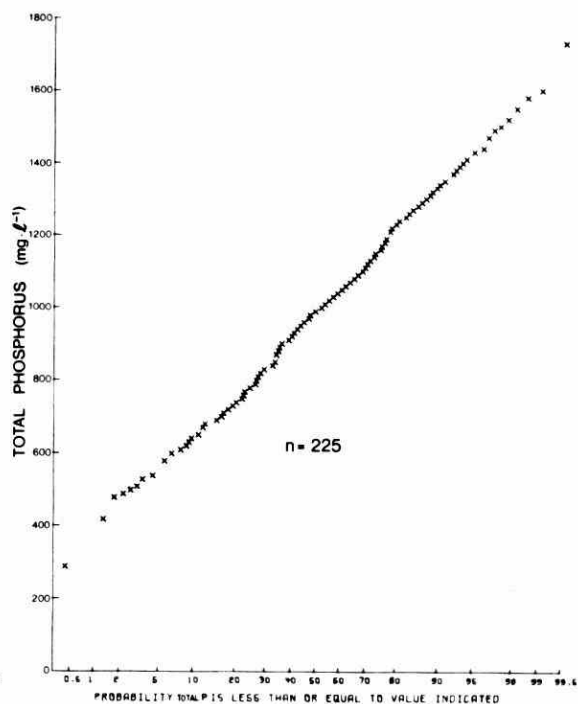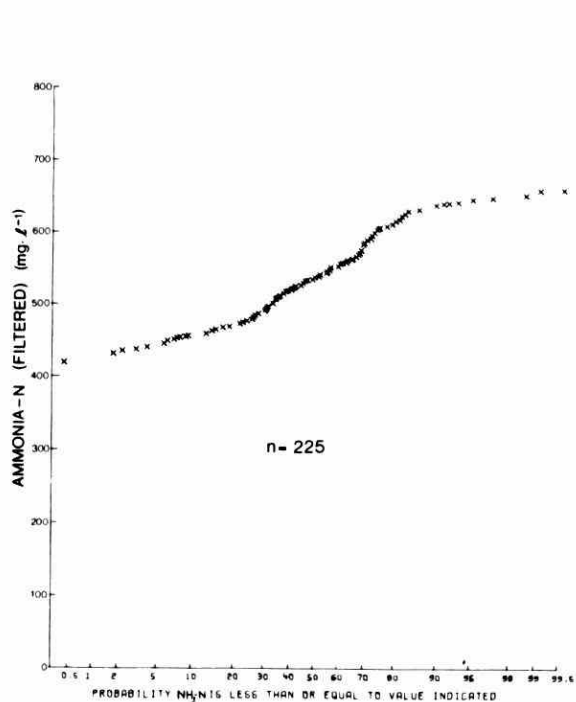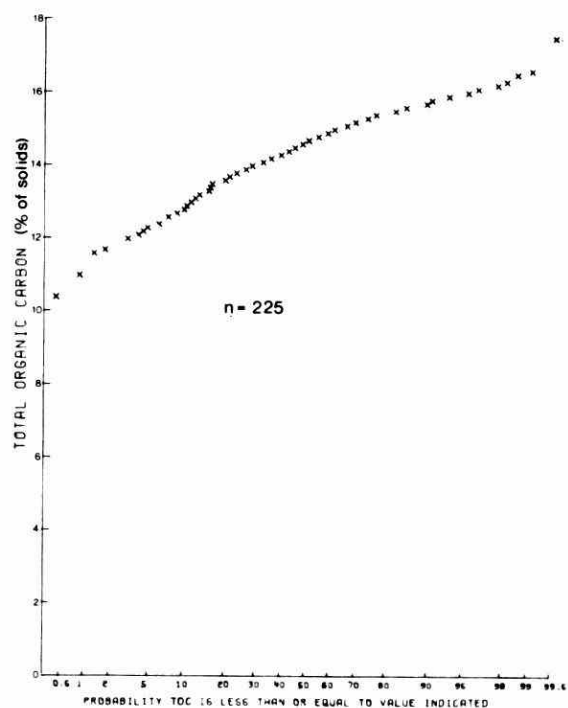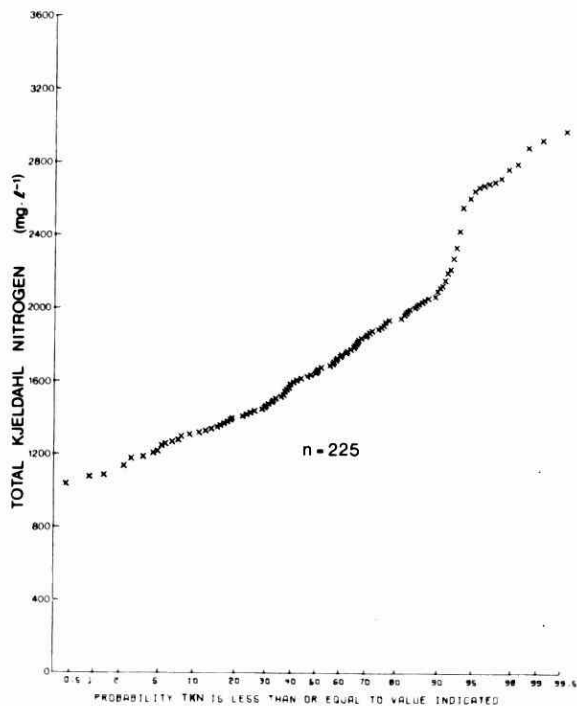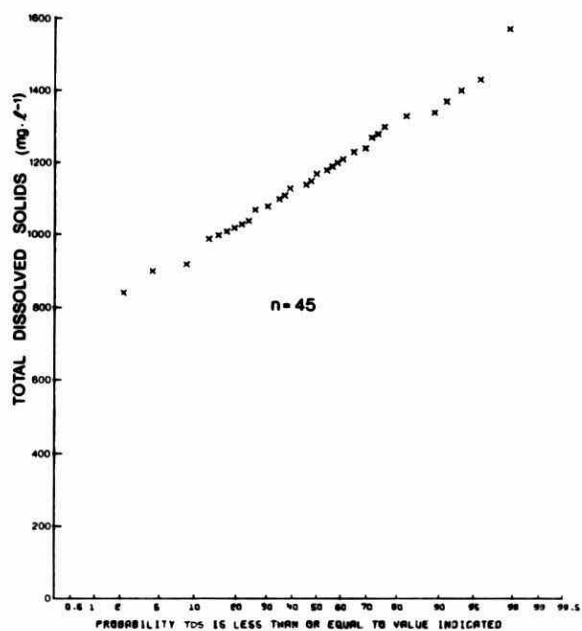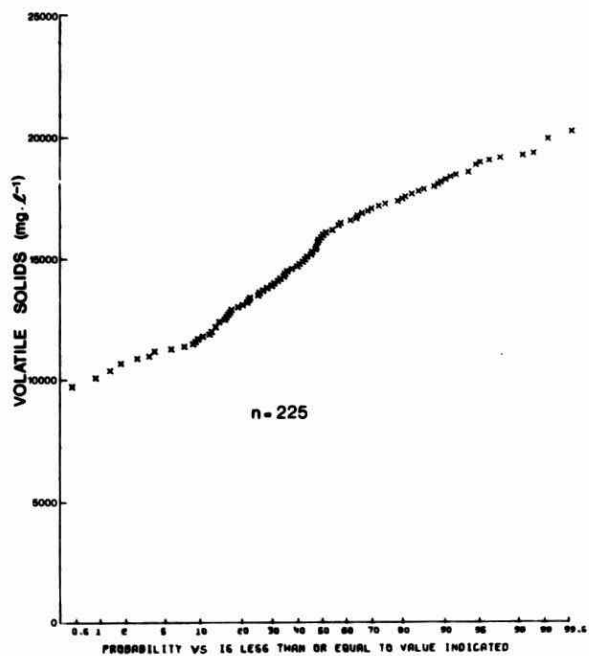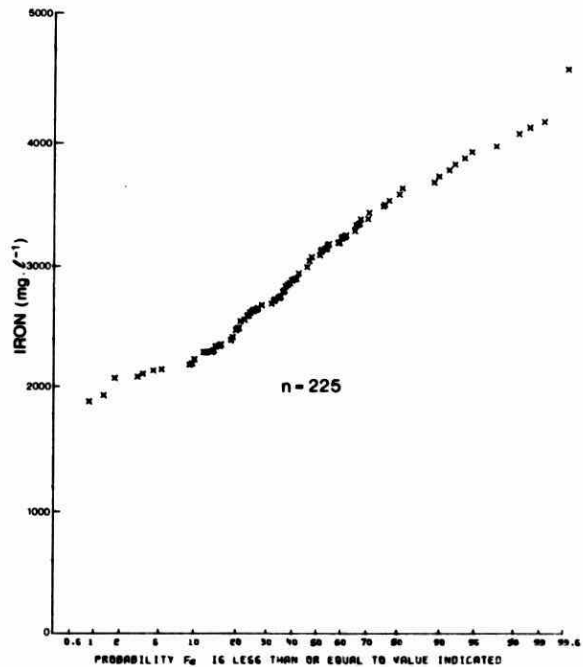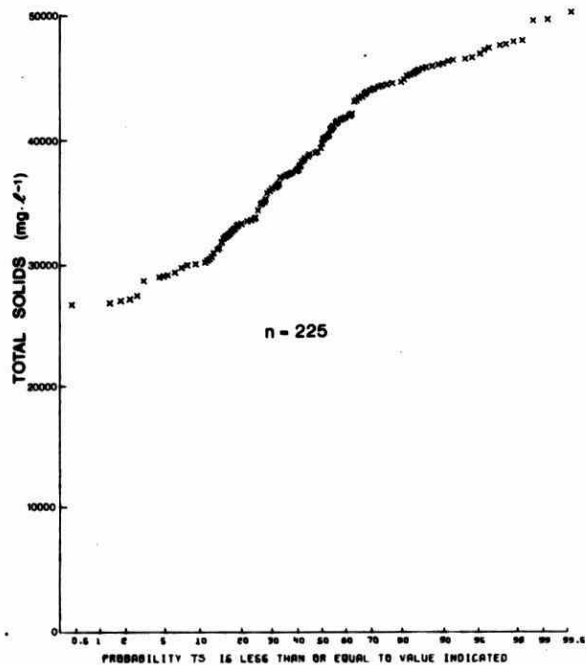
CHATHAM SLUDGE   MARCH 3-21, 1975

CHATHAM SLUDGE   MARCH 3-21, 1975

CHATHAM LONG TERM   JUNE—NOVEMBER, 1975

TOTAL KJELDAHL NITROGEN   (mg·l^{-1})

n = 99

PROBABILITY TKN IS LESS THAN OR EQUAL TO VALUE INDICATED

AMMONIA-N(mg·l^{-1})

n = 99

PROBABILITY NH₄-N IS LESS THAN OR EQUAL TO VALUE INDICATED

TOTAL SOLIDS (%wt.)

n = 99

PROBABILITY TS IS LESS THAN OR EQUAL TO VALUE INDICATED
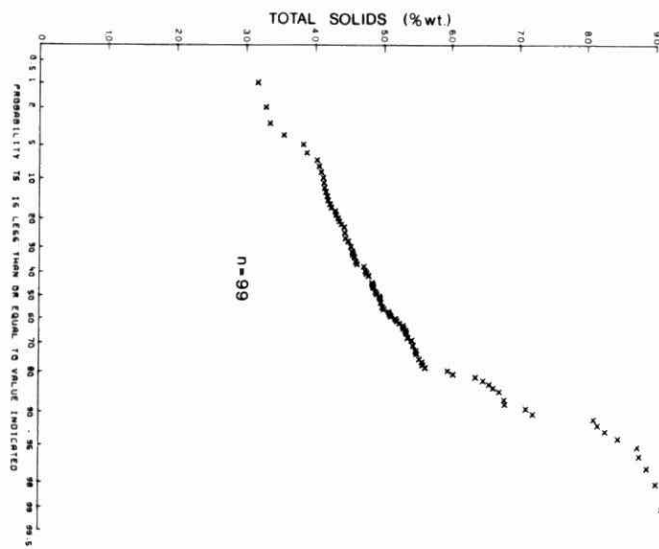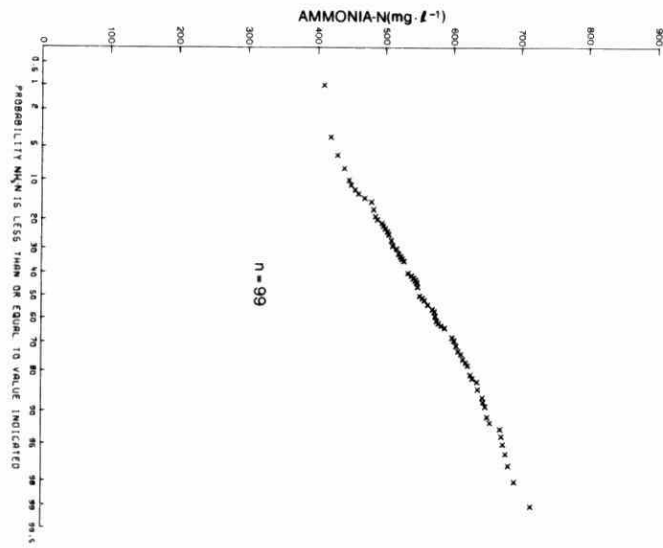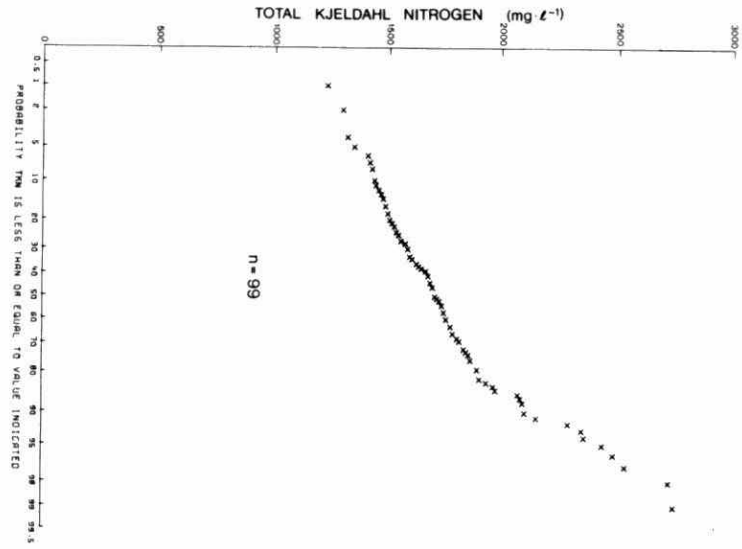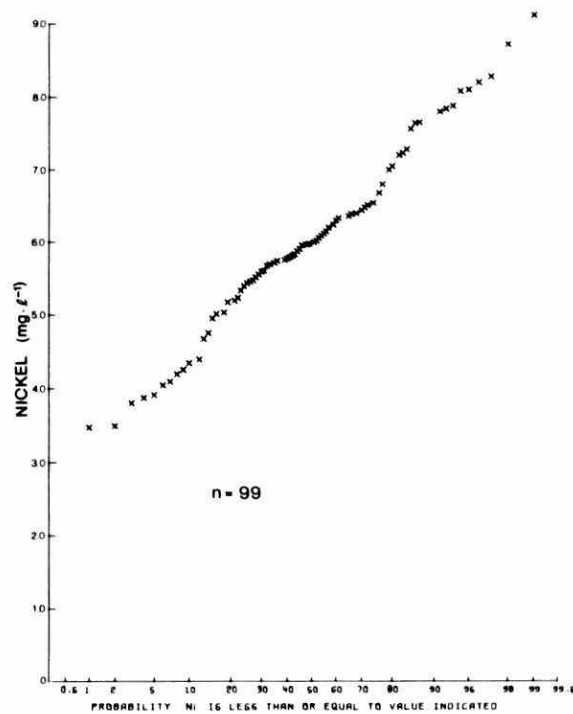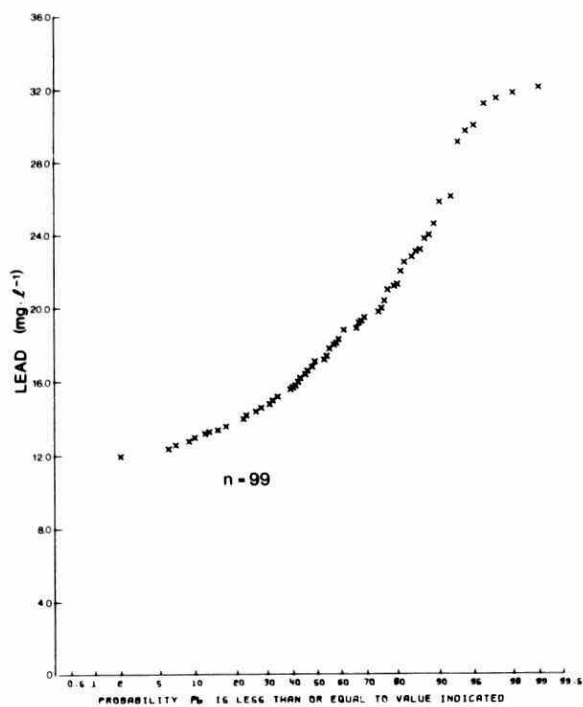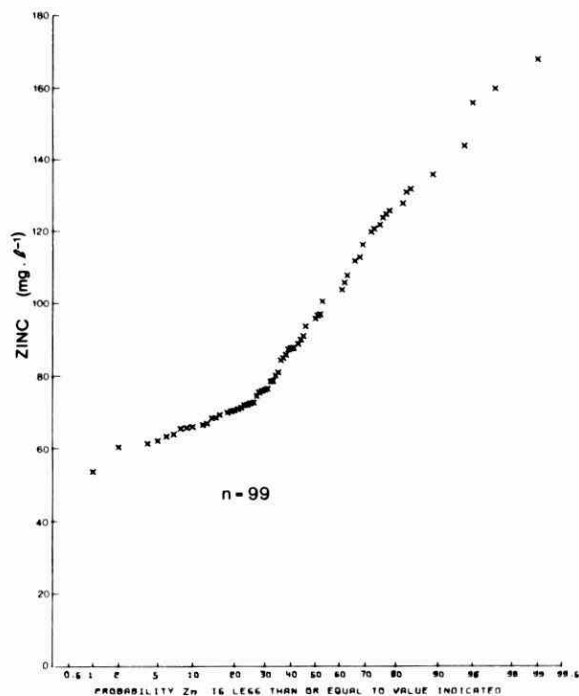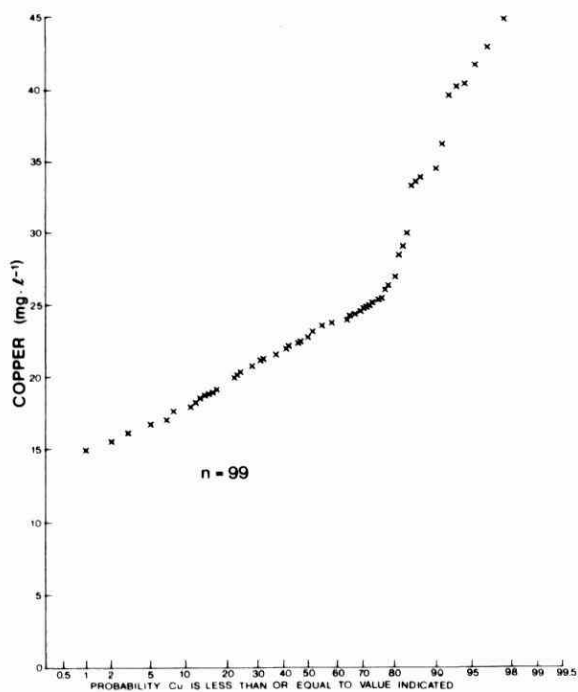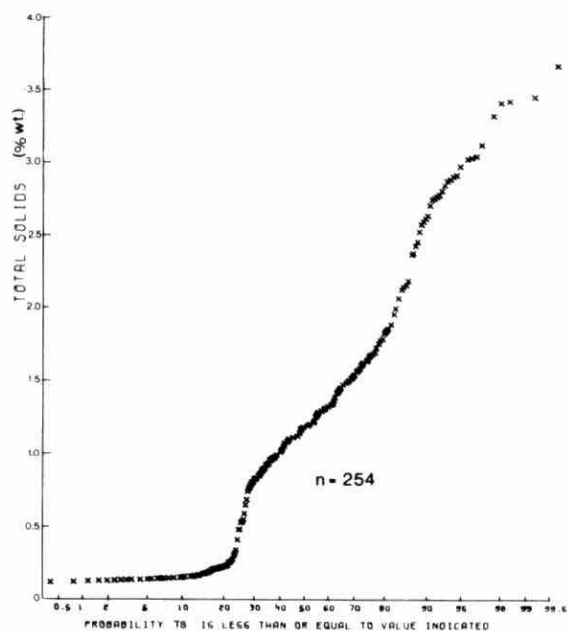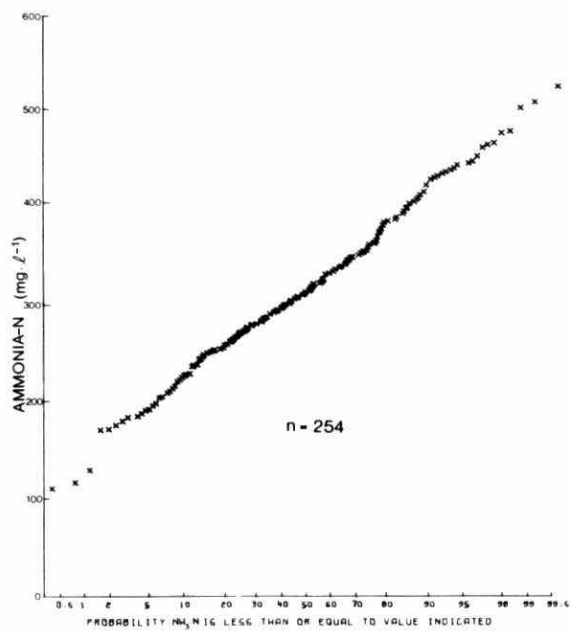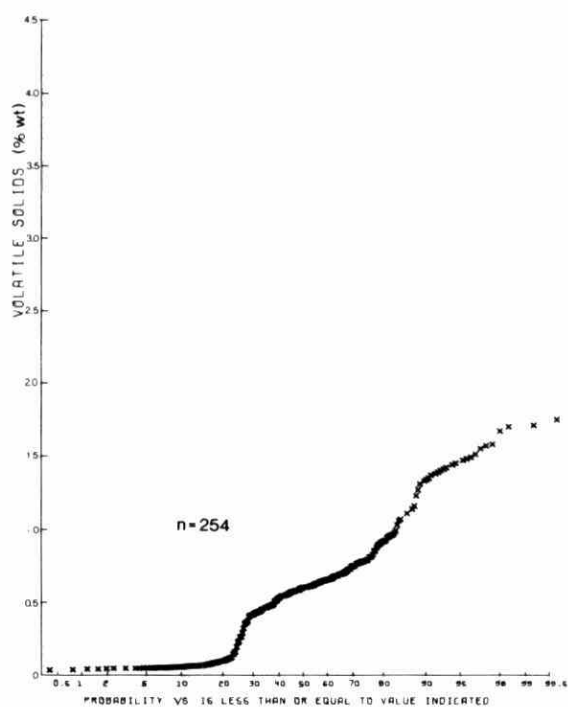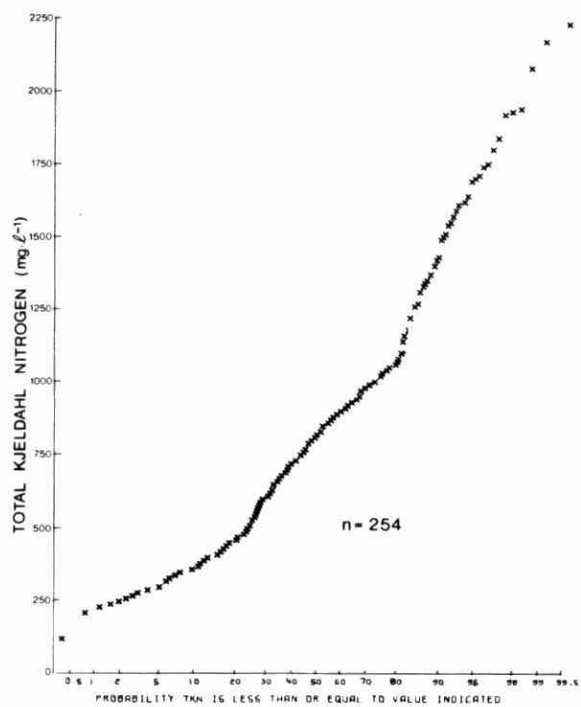
CHATHAM LONG TERM   JUNE – NOVEMBER, 1975

MILTON SLUDGE   JUNE 23 – JULY 31, 1975

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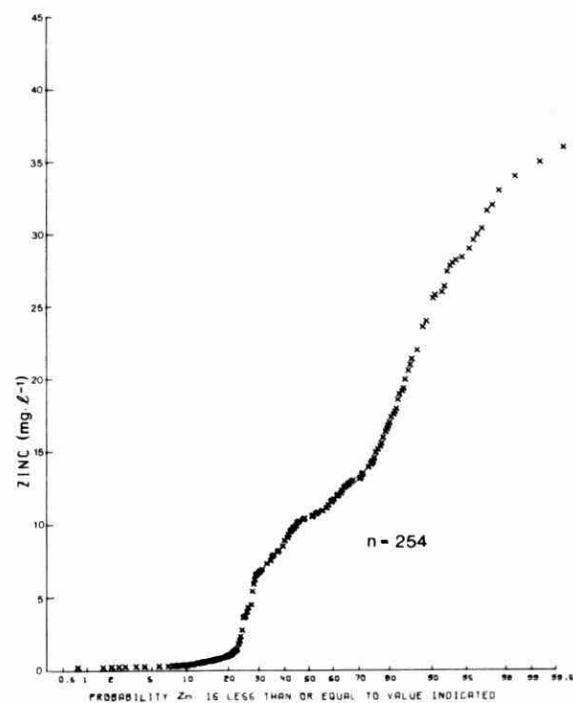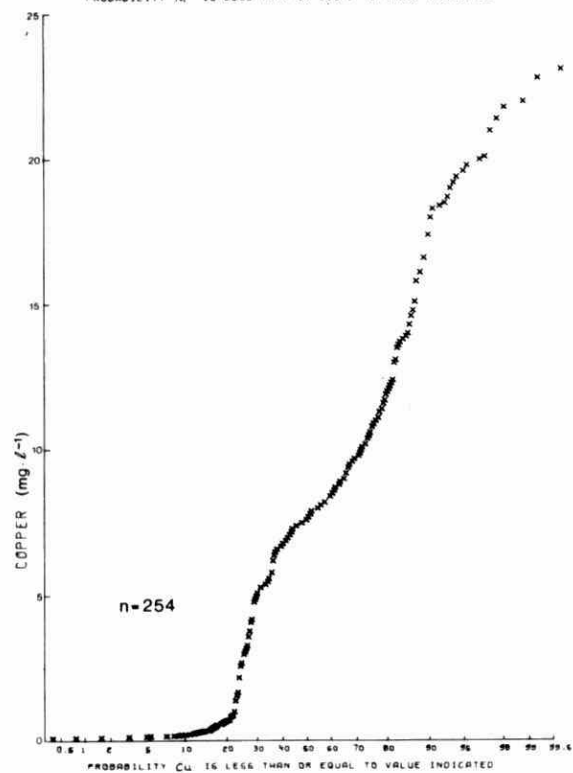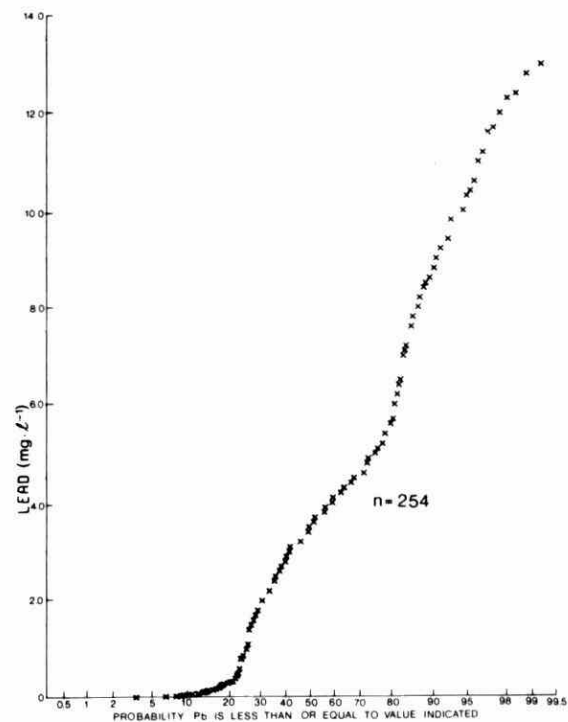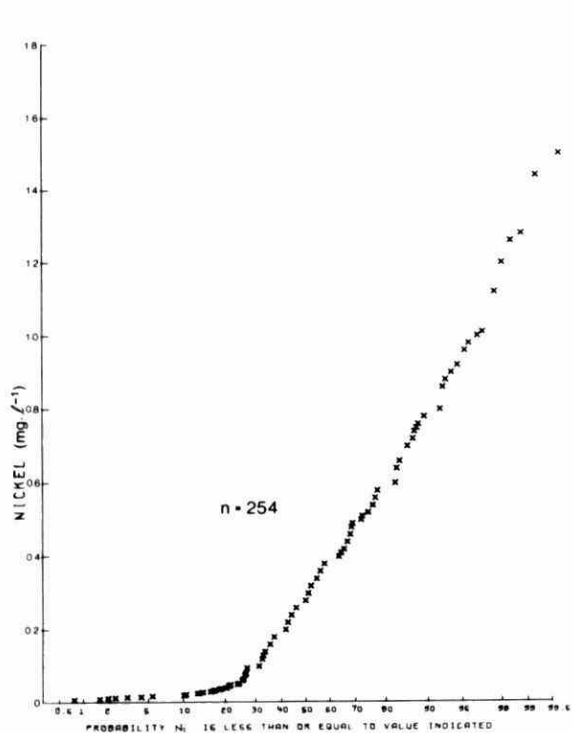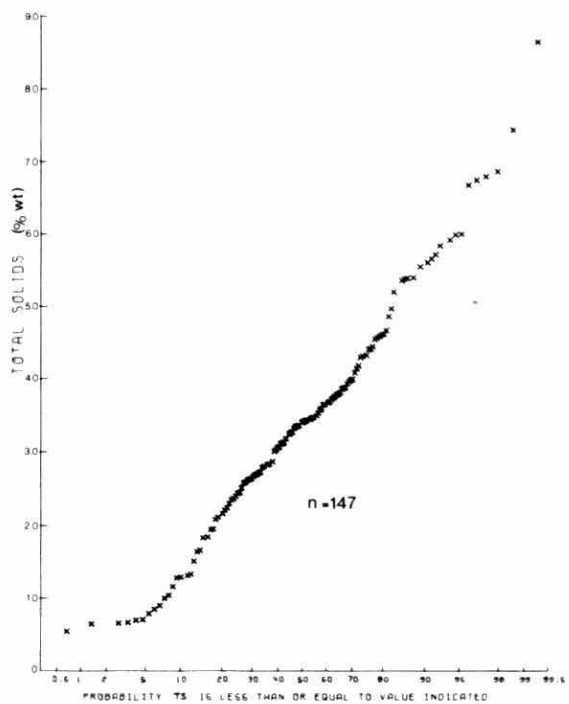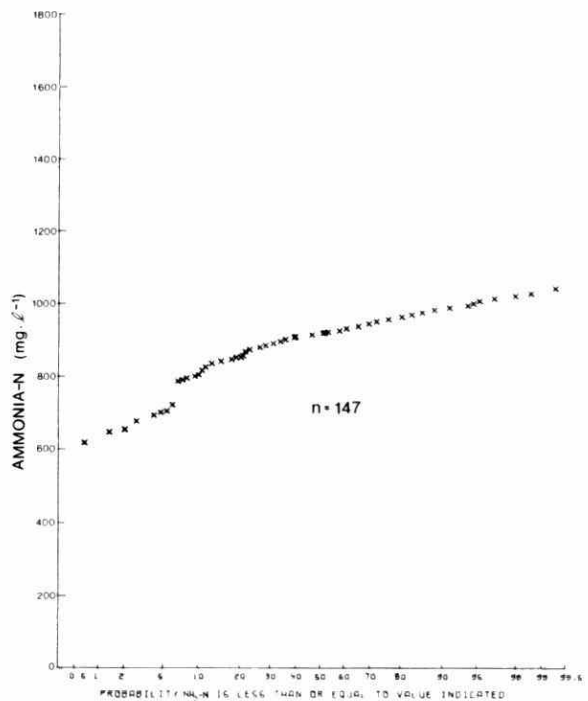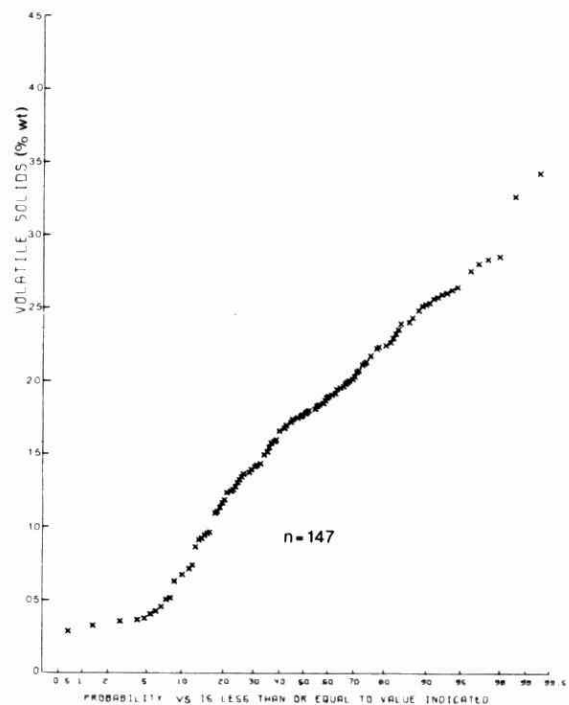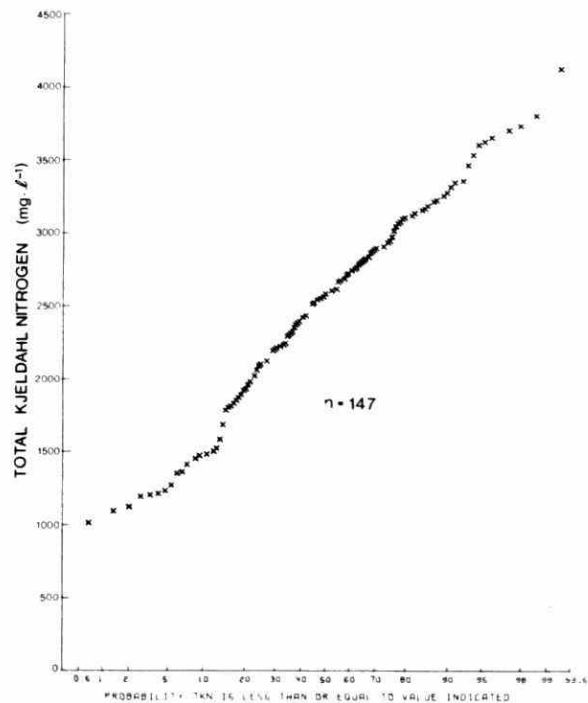
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OAKVILLE S.E. SLUDGE   JULY 16 – SEPT. 10, 1975

119
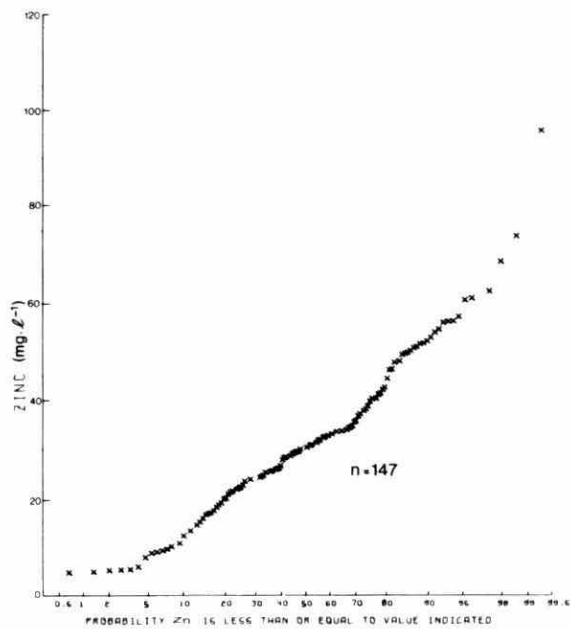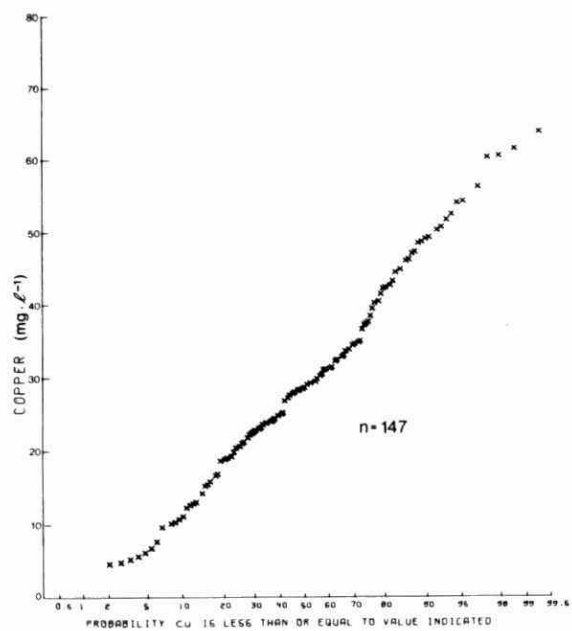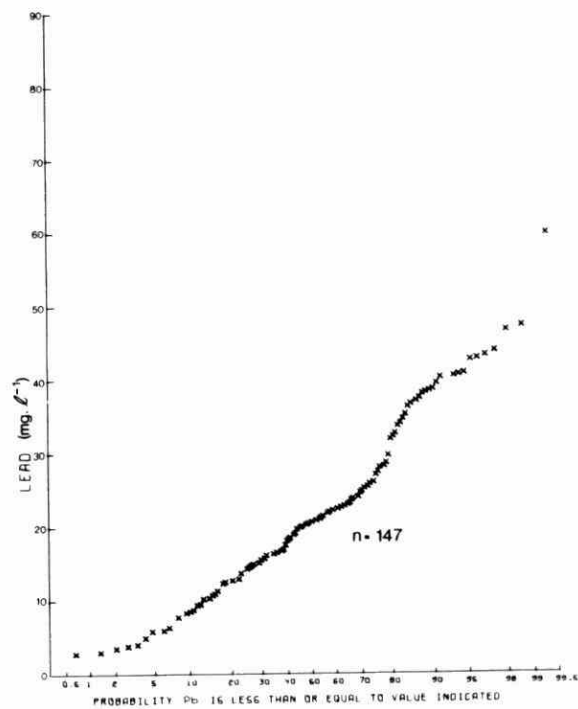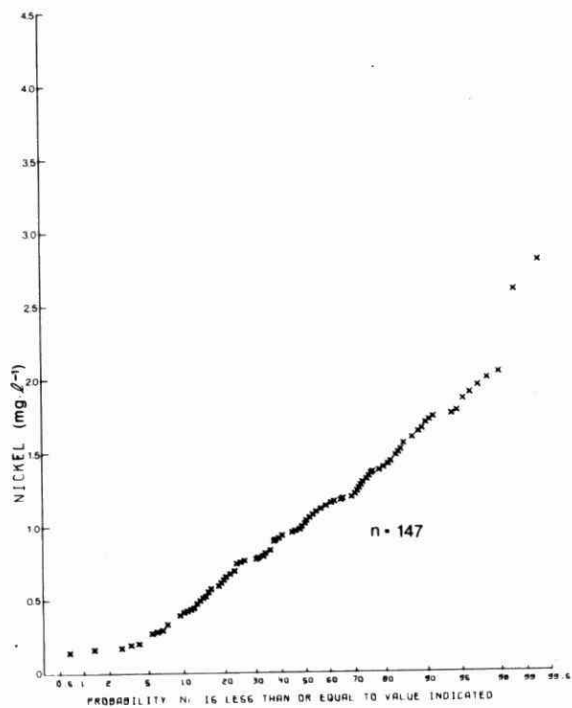
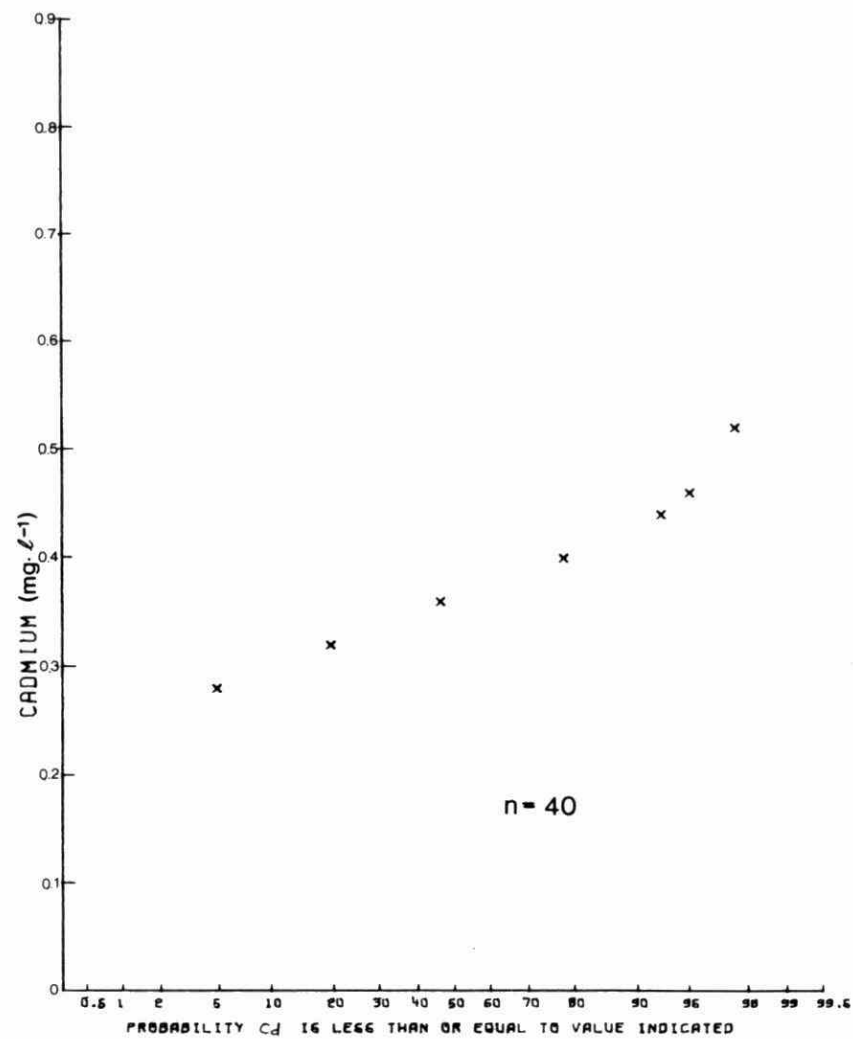OAKVILLE S.E. SLUDGE   JULY 16 – SEPT. 10, 1975
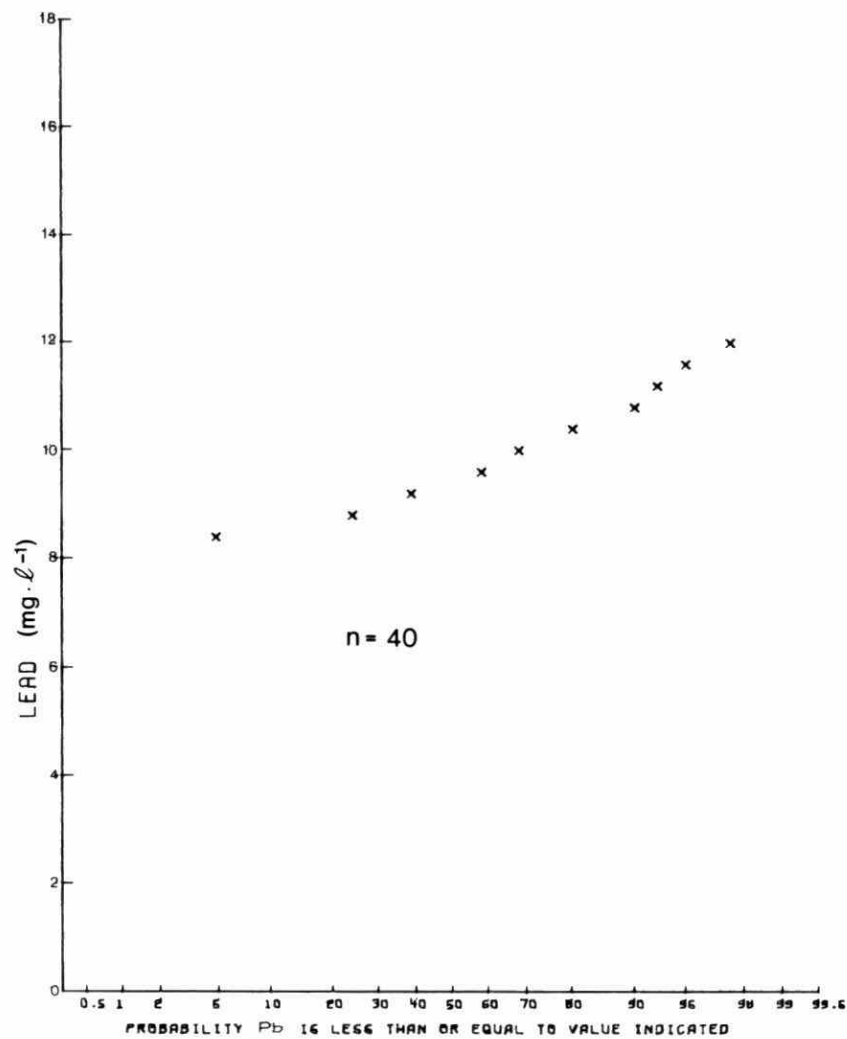
TILLSONBURG SLUDGE   OCTOBER 1974

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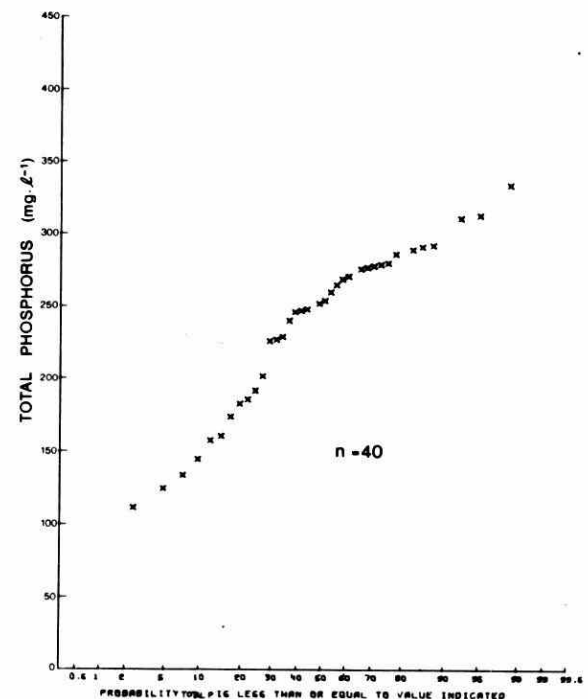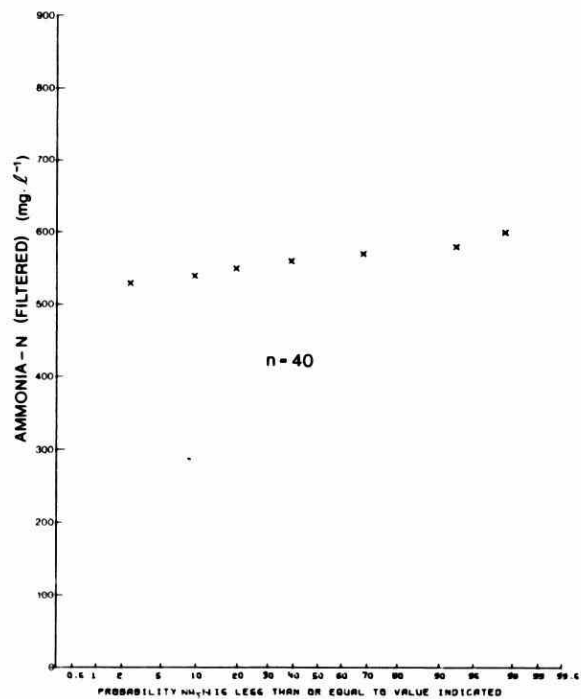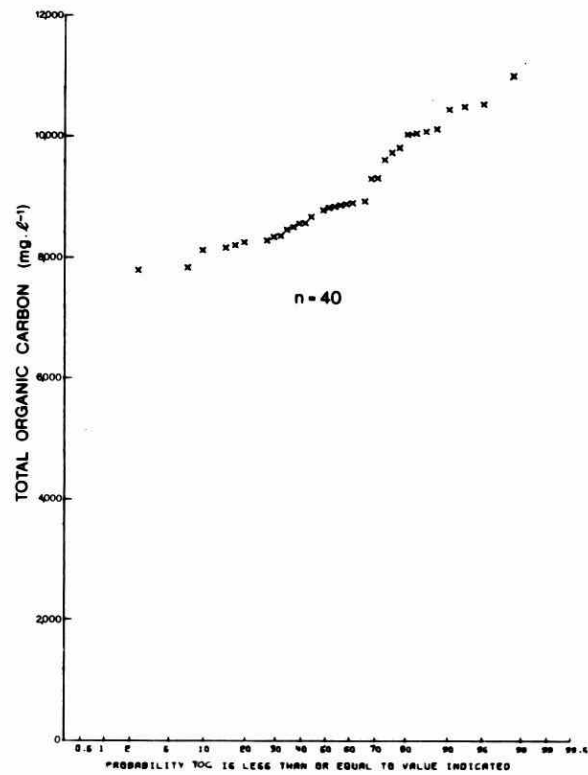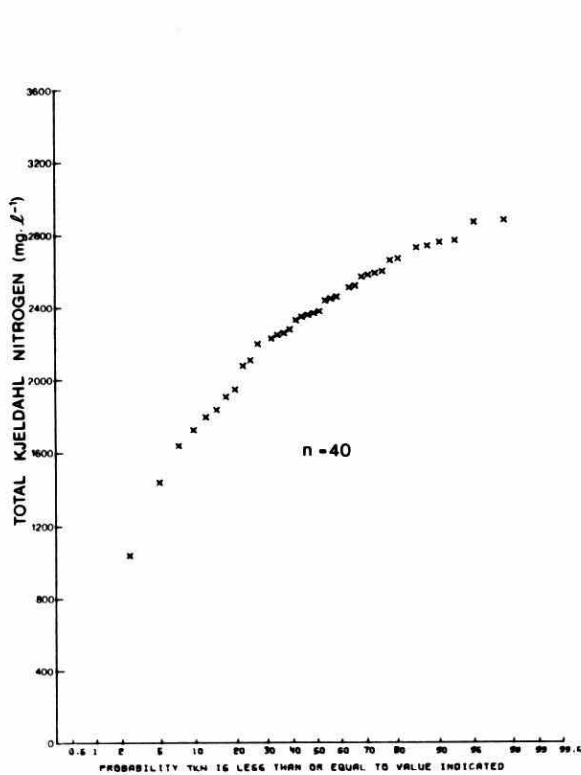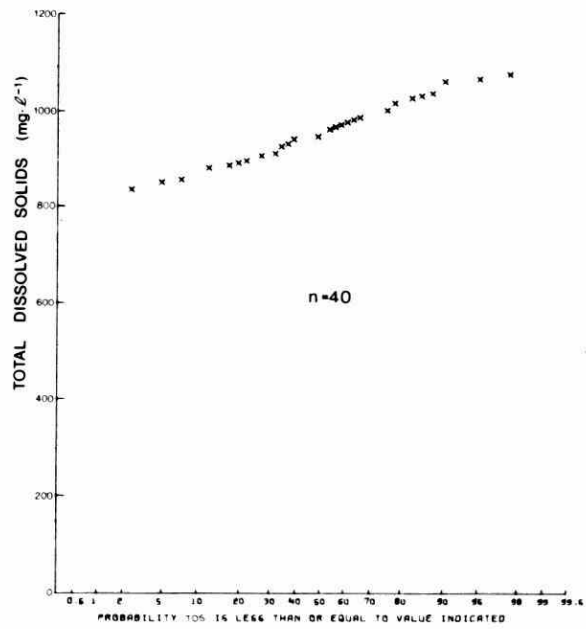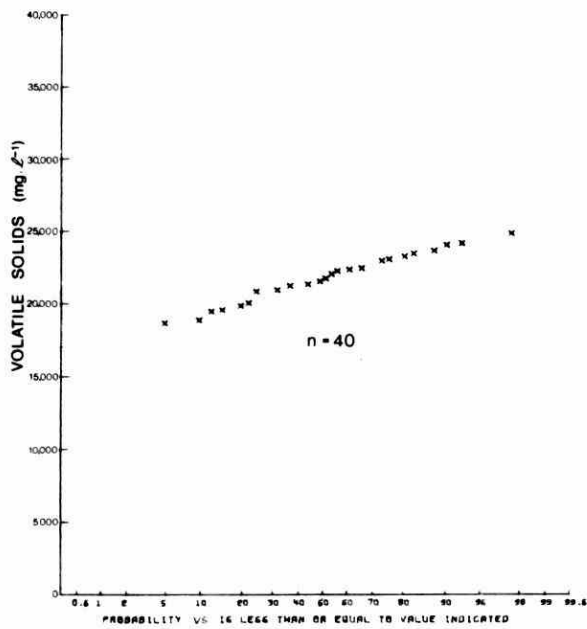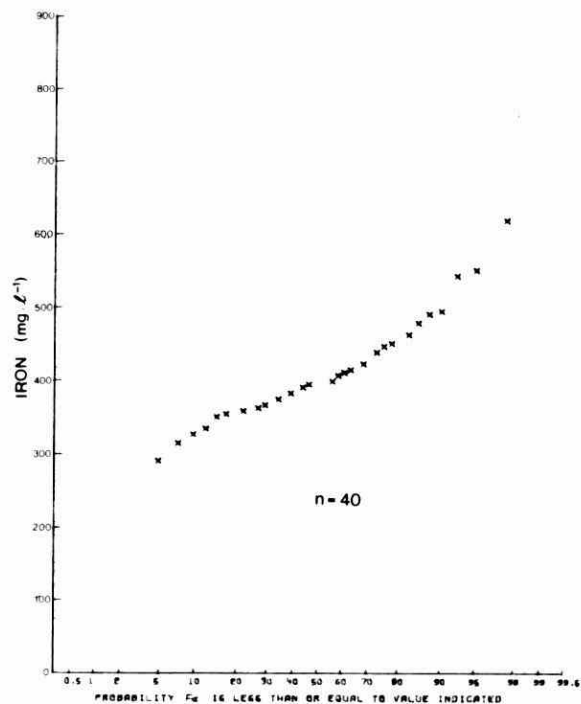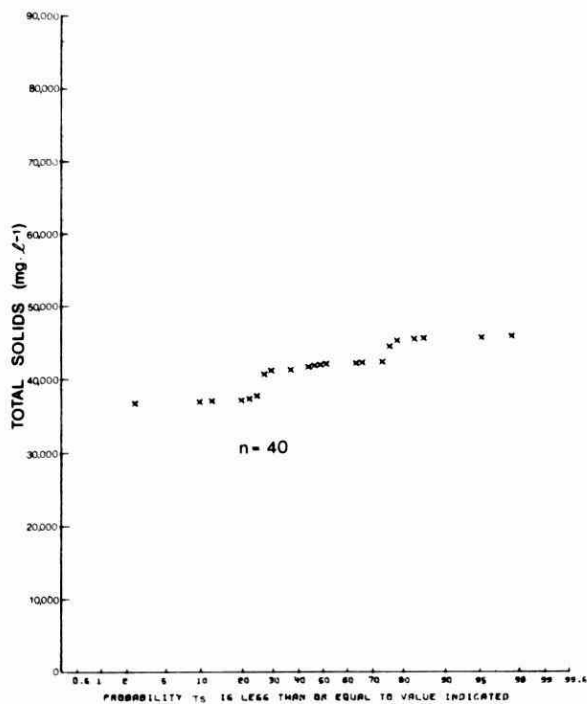
TILLSONBURG SLUDGE   OCTOBER 1974

TILLSONBURG SLUDGE OCTOBER 1974

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TILLSONBURG SLUDGE   OCTOBER 1974